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PART I.

Organic Chemistry.

Bromine Derivatives of Tetramethylmethane. Petru Poni (*Ann. sci. Univ. Jassy*, 1905, 3, 212—216).—Below 0°, the interaction in diffuse daylight between water, bromine, and ββ-dimethylpropane containing some β-methylpropane requires from four to fourteen days according to the intensity of the light. In addition to β-bromo-β-methylpropane, the following substances were isolated by fractional distillation under reduced pressure. *a-Bromo-ββ-dimethylpropane*, $CMe_3 \cdot CH_2Br$, is a colourless liquid with an ethereal odour, which boils at 89—91° under 749 mm. pressure. It has the sp. gr. 1·294 at 0°/0° and n_D 1·43689 at 20·4°.

β-Bromo-β-methylbutane has been obtained previously by Tissier.

aa-Dibromo-ββ-dimethylpropane, $CMe_3 \cdot CHBr_2$, is a colourless liquid with a strong ethereal odour, which boils at 64—65° under 43 mm. and decomposes when heated under the ordinary pressure. It has the sp. gr. 1·7883 at 0°/0° and n_D 1·50848.

aγ-Dibromo-ββ-dimethylpropane, $CH_2Br \cdot CMe_2 \cdot CH_2Br$, boils at 82—83° under 49 mm. and decomposes when heated under the ordinary pressure, has the sp. gr. 1·7052 at 0/0°, and n_D 1·50903 at 20·3°.

The constitution of the last two isomeric compounds is deduced from the law that the boiling point of a disubstituted derivative is the lower the nearer the substituents are together (Henry). C. S.

Preparation of Racemic Amyl Alcohol. Paul Freundler and E. Damond (*Compt. rend.*, 1905, **141**, 830—831).—Racemic amyl alcohol, obtained in small quantities by Herzig by reducing tiglic aldehyde (Abstr., 1882, 594) and by Frankland by racemisation of the active alcohol (compare Trans., 1897, **71**, 255), can be readily prepared by the condensation of trioxymethylene and magnesium *sec.*-butyl bromide (compare Locquin, Abstr., 1904, i, 546), the yield being 60 per cent. of the theoretical when the calculated quantity of trioxymethylene is added to the magnesium *sec.*-butyl bromide suspended in ether to which a few drops of carbon disulphide have been added to moderate the action, and thus avoid the formation of butylene and butane (compare Bischoff, Abstr., 1905, i, 589; Ahrens and Stapler, *ibid.*, 868). *sec.*-Butyl bromide is obtained by the action of phosphorus tribromide on *sec.*-butyl alcohol, prepared by the direct hydrogenation of methyl ethyl ketone at 140° by the method of Sabatier and Senderens (compare Abstr., 1903, i, 733). M. A. W.

Solubility of Various Salts in Ethylene Glycol. William Oechsner de Coninck (*Bull. Acad. roy. Belg.*, 1905, 275—276, 359).—The solubilities of a number of inorganic salts in ethylene glycol, having the composition $C_2H_6O_2,H_2O$, at temperatures about 15°, are tabulated. F. G. C. S.

Action of Light on a Solution of Uranyl Sulphate in Ethylene Glycol. William Oechsner de Coninck (*Bull. Acad. roy. Belg.*, 1905, 360).—Uranyl sulphate is dissolved in a small quantity of water, excess of ethylene glycol added, and the whole placed in a flask exposed to sunlight. In two hours, the liquid is quite green, and in $2\frac{1}{2}$ hours uranous sulphate is precipitated. In glycerol, no such action takes place, and even after fifteen months' exposure only a slight green coloration is obtained. This reaction serves to distinguish between ethylene glycol and glycerol. F. G. C. S.

Cetylphosphoric Acid. Joachim Biehringer (*Ber.*, 1905, **38**, 3974—3977. Compare Tüttscheff, *Jahresb.*, 1860, 405).—*Cetyl dihydrogen phosphate* (*cetylphosphoric acid*), $C_{16}H_{33}O\cdot PO(OH)_2$, is readily obtained by the action of phosphoric oxide on a solution of cetyl alcohol in dry ether. The ester is not produced in the absence of ether at the same temperature. It forms a snow-white, crystalline powder, is extremely hygroscopic, softens at 60°, and melts at 74°. It dissolves readily in most organic solvents, and reacts as a dibasic acid when titrated with alcoholic potash, using phenolphthalein as indicator.

Sodium, *lithium*, *ferric*, *lead*, and *silver* salts have been prepared. The salts of the alkaline earths are sparingly soluble. J. J. S.

Action of Ammonia and Amines on Allyl Formate. Pieter van Romburgh (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, **8**, 138—141. Compare Abstr., 1882, 378).—Allyl formate may be prepared conveniently by heating a mixture of glycerol with an equal weight of concentrated formic acid at 125° and finally at 240°; at the higher temperature, a mixture of allyl formate, allyl alcohol, and a small amount of formic acid distils over, and this is subjected to fractional distillation.

Allyl formate reacts with anhydrous ammonia, slowly if pure, more quickly in presence of a small quantity of allyl alcohol, with development of heat and formation of formamide which melts at 2·4°.

Primary and secondary fatty amines, benzylamine, phenylhydrazine, and piperidine react with allyl formate to form substituted formamides, the rise in temperature being greatest with the primary amines, whilst the reaction with phenylhydrazine takes place without change of temperature.

*Form*iso*butylamide* boils at 229°. Formobenzylamide melts at 62° and not at 49°, as stated by Holleman (Abstr., 1895, i, 457). *Formodi*iso*butylamide* boils at 227—228° (corr.). G. Y.

Action of Ammonia and Amines on Formic Esters of Glycols and Glycerol. II. PIETER VAN ROMBURGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, **8**, 339—341).—When ammonia gas is absorbed by ethylene diformate, a considerable development of heat occurs, and the product on distillation yields ethylene glycol and somewhat impure formamide. Substituted ammonias (dipropylamine, benzylamine) give pure substituted formamides in very good yield. Similar reactions take place between propylene $\alpha\beta$-diformate, or the formins of glycerol, and ammonia, dimethylamine, dipropylamine, di*iso*butylamine, benzylamine, or piperidine, the distillation being performed in a vacuum.

[With W. VAN DORSSEN.]—The reaction is applicable to the formic esters of unsaturated glycols, formobenzylamide having been obtained by distilling a mixture of benzylamine and $\gamma\delta$-dihydroxy-$\Delta^{\alpha\epsilon}$-hexadiene diformate. C. S.

Acetic Arsenious Anhydride. AMÉ PICTET and A. BON (*Bull. Soc. chim.*, 1905, [iii], **33**, 1139—1143. Compare Abstr., 1903, i, 309, 601).—*Triacetic arsenious anhydride*, $As(OAc)_3$, prepared by dissolving arsenious oxide in acetic anhydride, crystallises in colourless needles, melts at 82°, distils at 165—170° under 31 mm. pressure, is readily soluble in chloroform or ethyl acetate, less so in cold benzene, and almost insoluble in light petroleum or carbon disulphide. It decomposes in moist air forming the two corresponding acids, and is attacked by alcohols yielding the corresponding alkyl arsenite and acetate. Glyceryl and phenyl arsenites were prepared in this way.

When fused with benzoic acid, triacetic arsenious anhydride furnishes acetic acid and *tribenzoic arsenious anhydride*, $As(OBz)_3$. This occurs as a white, crystalline mass, melts at 155°, and decomposes rapidly on exposure to air, forming benzoic and arsenious acids. It dissolves readily in chloroform, less so in benzene or ethyl acetate, and very little in light petroleum or carbon disulphide. T. A. H.

Preparation of Anhydrides of Monobasic Acids. VEREIN FÜR CHEMISCHE INDUSTRIE (D.R.-P. 161882).—Acid anhydrides are readily prepared by the action of sulphuryl chloride on the alkali salts of the corresponding acids, but large quantities of acid chloride are obtained when alkaline earth salts are substituted. It is found, however, that a mixture of the two salts gives satisfactory results, even 10—15 per cent. of sodium acetate mixed with calcium acetate being sufficient to prevent the formation of acetyl chloride.

C. H. D.

Crotonic and *iso*Crotonic Acids. William Oechsner de Coninck (*Bull. Acad. roy. Belg.*, 1905, 274—275. Compare Abstr., 1905, i, 321, 628).—Crotonic acid dissolves in warm sulphuric acid and becomes charred, *iso*crotonic acid forms a light brown solution becoming dark brown, garnet-red, and black, depositing a flocculent precipitate of carbon.

On heating gradually with a large excess of sulphuric acid, both acids char and evolve carbon dioxide and then sulphur dioxide.

F. G. C. S.

Preparation of Oxalates from Formates. Rudolf Koepp & Co. (D.R.-P. 161512).—The conversion of formates into oxalates by heat takes place quantitatively when about 1 per cent. of alkali hydroxide is added to the mass before heating. The alkali appears to exert a catalytic influence. In the case of sodium formate containing 1 per cent. of sodium hydroxide, evolution of hydrogen begins at 290°, and at 360° the mass is completely converted into white, porous oxalate. Alkali peroxides, plumbates, amides, ethoxides, or phenoxides may also be used.

C. H. D.

Ester Anhydrides of Dibasic Acids. D. Mol (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, **8**, 336—337).—*Ethyl anhydro-oxalate*, $O(CO{\cdot}CO_2Et)_2$, obtained by the action of ethyloxalyl chloride on potassium ethyl oxalate covered with ether, distils at 85—90° under less than 1 mm. pressure; the distillate solidifies on cooling and melts at 4°. The anhydride, which is also obtained by acting on an excess of potassium ethyl oxalate with phosphorus oxychloride, decomposes when heated at the ordinary pressure.

C. S.

Derivatives of Trimethylparaconic and Camphoronic Acids. William A. Noyes and Howard W. Doughty (*J. Amer. Chem. Soc.*, 1905, **27**, 1429—1435).—Noyes and Patterson (Abstr., 1902, i, 742) have shown that when ethyl trimethylitamalate is treated with phosphorus tribromide, it is converted into ethyl trimethylparaconate. As the ester used in this experiment was not pure, it was considered desirable to ascertain the action of phosphorus tribromide on methyl trimethylitamalate. *Methyl trimethylitamalate* was obtained as a yellow oil which boils at 122—127° under 12—14 mm., and at 261—265° under atmospheric pressure. When this ester was treated with hydrobromic acid or phosphorus tribromide, methyl trimethylparaconate could not be obtained. Attempts to prepare an acetyl or a benzoyl derivative of the ester were unsuccessful. It was found impossible to reduce trimethylparaconic acid electrolytically, the acid being recovered from the experiments unchanged.

When ethyl trimethylsuccinate is heated with ethyl chloroacetate in presence of sodium or sodium ethoxide, no trace of camphoronic acid is produced. Attempts were made to effect the condensation of chloral with sodium trimethylsuccinate, but without success.

i-*Bromoanhydrocamphoronic chloride*, obtained by the method used by Aschan (Abstr., 1895, i, 188) in the preparation of the active form, crystallises from ether, and melts at 123—126°. i-*Camphoranic anhydride* distils at 193—194° under 20 mm. pressure, solidifies as a white, crystalline mass, melts at 119—121°, and is readily soluble in water and sparingly so in ether. i-*Camphoranic acid* crystallises in pyramids, and, on heating, partly sublimes and melts at 190—191°.

E. G.

Trithioformaldehyde and a New Method of preparing Trimethylsulphonium Iodide. ALBERT REYCHLER (*Bull. Soc. chim.*, 1905, [iii], **33**, 1226—1232. Compare Klinger, Abstr., 1879, 132).—Trithioformaldehyde may be purified by recrystallisation from hot aniline and subsequently washing with hydrochloric acid and alcohol. It reacts with methyl iodide when a mixture of the two substances is heated in closed vessels at 80° to 100°, forming trimethylsulphonium iodide; the yield of the latter under these conditions is small, and the reaction goes better in presence of methyl alcohol, when a yield of trimethylsulphonium iodide equivalent to from 85 to 90 per cent. of the theoretical is obtainable. The reaction may be represented by the following equations: $(CH_2S)_3 + 3MeI + 6MeOH = 3SMe_3I + 3CH_2(OH)_2$ and $3CH_2(OH)_2 + 6MeOH = 6H_2O + 3CH_2(OMe)_2$. The presence of methylal in the by-products of the reaction was proved.

The reaction becomes much more complex when ethyl iodide is substituted for methyl iodide or ethyl alcohol for methyl alcohol.

The author notes that this breaking down of the molecule of trithioformaldehyde by such a reagent as methyl iodide is remarkable in view of the stability of the polymeride towards other reagents.

T. A. H.

Crystals of *s*-Tetrachloro*iso*propylformal. F. KAISIN (*Bull. Acad. roy. Belg.*, 1905, 276—277).—A correction to a former paper (Abstr., 1905, i, 261). The crystallographic data for *s*-tetrachloro*iso*propylformal should be [$a:b:c = 2·789:1:1·384$]. F. G. C. S.

Action of Hydrogen Cyanide on Ketones. A. J. ULTEE (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, **8**, 141—144).—Acetone and hydrogen cyanide react in aqueous solution in presence of a small quantity of a base with development of heat to form the cyanohydrin (hydroxy*iso*butyronitrile), which, as the reaction is reversible, can be isolated by distillation only after neutralisation of the base. That the same equilibrium is reached by adding a trace of potassium hydroxide to a molecular mixture of acetone and hydrogen cyanide or to the cyanohydrin in aqueous solution is proved by the refractions n_D 1·39721 and 1·39818 at 12° for the two solutions respectively. Determinations of the free hydrogen cyanide present show that the amount of the cyanohydrin formed at 0° is 94·5, and at 25° is 88·60 per cent. of the theoretical. The corresponding values for methyl ethyl ketone are 95·57 and 90·36, for diethyl ketone 95·90 and 91·29 per cent. respectively.

On mixing anhydrous hydrogen cyanide with anhydrous acetone, there is a slight rise in temperature, but no interaction takes place even after six months, as shown by determinations of the free hydrogen cyanide present and by the unchanged refraction of the mixture. Pure cyanohydrins may be obtained by adding a slight excess of fuming hydrochloric acid to potassium cyanide covered by a ketone and distilling the product under reduced pressure.

Hydroxy*iso*butyronitrile melts at −19·5° to a colourless liquid which boils at 82° under 23 mm., decomposes on distillation under the atmospheric pressure, and has the sp. gr. 0·9342 at 18° and n_D 1·40526 at 8·5°.

α-Hydroxy-α-methylbutyronitrile, from methyl ethyl ketone, is a colourless liquid having a faint ketonic odour, boils at 91° under 20·5 mm., does not solidify in a paste of solid carbon dioxide and acetone, and has the sp. gr. 0·9324 at 18·5° and n_D 1·41775 at 12·5°.

α-Hydroxy-α-ethylbutyronitrile, prepared from diethyl ketone, is a colourless liquid which boils at 97·5° under 18·5 mm. pressure, does not solidify when cooled with solid carbon dioxide and acetone, and has the sp. gr. 0·9300 at 18·5° and n_D 1·42585 at 18°. G. Y.

Triacetylcellulose. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 159524. Compare Skraup, Abstr., 1899, i, 852; Franchimont, Abstr., 1900, i, 141).—Acetic anhydride and sulphuric acid act on cellulose below 50°, preferably in presence of glacial acetic acid, to form *triacetylcellulose.* The product dissolves readily in chloroform, epichlorohydrin, nitrobenzene, or acetic acid, but is insoluble in alcohol, ether, glycerol, or amyl acetate. It decomposes at about 250°, and is very resistant towards alkali hydroxides or dilute acids. On evaporation of its solutions, it forms colourless films which are perfectly flexible even at a thickness of 0·5 mm., and do not become brittle with time. Very voluminous gelatinous masses are obtained when the concentrated solutions are poured into water or alcohol. C. H. D.

Action of Bromine on Trimethylamine. James F. Norris (*Ber.*, 1905, **38**, 3904—3906).—Hantzsch and Graf's product, obtained by the action of bromine on trimethylamine (Abstr., 1905, i, 575), is not identical with Remsen and Norris' trimethylamine dibromide (Abstr., 1896, i, 336), which melts at 117—119° and for which the formula NMe_3,HBr,Br is now confirmed (Abstr., 1898, i, 169). The author considers that Hantzsch and Graf's substance may be the primary reaction-product, which changes easily into Remsen and Norris' dibromide. G. Y.

Conversion of Formhydroxamic Acid into Fulminic Acid. Henry C. Biddle (*Ber.*, 1905, **38**, 3858—3859. Compare Abstr., 1900, i, 137).—A reply to Wöhler (Abstr., 1905, i, 419). In order to secure the conversion of chloro-formoxime acetate by the action of silver nitrate into silver fulminate, it is necessary to allow the mixed solutions to remain for twenty-four hours; the silver fulminate is somewhat soluble in water and might be overlooked when the precipitate is digested with much boiling water. T. M. L.

Compounds of Metallic Thiocyanates with Organic Bases.

Hermann Grossmann and Fritz Hünseler (*Zeit. anorg. Chem.*, 1905, **46**, 361—405. Compare Abstr., 1904, i, 341).—The additive compounds, such as $Ni(SCN)_2,2C_6H_5{\cdot}NH_2$, were usually prepared by the action of an aqueous or alcoholic solution of the metallic thiocyanate on an alcoholic solution of the base, crystals in some cases separating at once.

The double salts, such as $Ni(NH_3Ph)_2(SCN)_3$, were usually prepared by dissolving the corresponding additive compounds in thiocyanic acid and evaporating the solution if necessary.

Pyridine mercuric thiocyanate, $Hg(SCN)_2,C_5H_5N$, forms colourless, transparent, monoclinic crystals. *Pyridiniummercuric thiocyanate*, $HgC_5H_6N(SCN)_3$, is a colourless, crystalline mass. *Pyridiniummercuric chloride*, $Hg(C_5H_6N)_2Cl_3$, and *bromide* form long, prismatic, triclinic crystals; the *iodide* long, slender, yellow, lustrous needles. *Pyridiniummercuric chlorobromide*, $HgBr_2,C_5H_6NCl$, occurs in long, prismatic, colourless, monoclinic crystals; the *chloroiodide*,

$$HgI_2,2C_5H_6NBr,$$

forms yellow, not well-defined crystals. $2HgI_2,3C_5H_6NCl$ occurs in four-sided, monoclinic prisms; the *chlorocyanide*, $3Hg(CN)_2,2C_6H_5NCl$, forms long, prismatic, monoclinic crystals.

Cobalt thiocyanate, $Co(SCN)_2,4H_2O$, forms glistening, wine-red, rhombic crystals which gradually become brown and opaque in the air (compare Rosenheim and Cohn, Abstr., 1901, i, 456).

Tetrapyridine cobalt thiocyanate, $Co(SCN)_2,4C_5H_5N$, crystallises in rose-coloured needles.

Tripyridiniumcobalt thiocyanate, $Co(C_5H_6N)_3(SCN)_5$, forms dark blue, monoclinic crystals, which show mixed colours. A *dipyridinium* compound can also be obtained. All complex cobalt thiocyanates are blue in alcoholic and concentrated aqueous solution, but are split up into their components by excess of water, the solution becoming rose-coloured.

Dipyridiniumnickel thiocyanate, $Ni(C_5H_6N)_2(SCN)_4$, forms green, hemispherical crystals.

Tetrapyridine ferrous thiocyanate, $Fe(SCN)_2,4C_5H_5N$, forms yellow, lustrous, prismatic crystals, which do not readily oxidise in the air. *Tripyridiniumferrous thiocyanate*, $Fe(C_5H_6N)_3(SCN)_5$, and the corresponding *manganous* compound, $Mn(C_5H_6N)_3(SCN)_5$, are obtained respectively in yellow crystals which slowly become red in the air and in well-defined, colourless crystals. The cobalt, ferrous, and manganous compounds are isomorphous.

Dipyridiniumzinc iodide, $Zn(C_5H_6N)_2I_4$, forms yellow, monoclinic crystals. *Pyridinium thiocyanate*, C_5H_6N,SCN, obtained by evaporating molecular amounts of its components, separates in transparent, odourless, hygroscopic crystals.

Quinoline cadmium thiocyanates, $Cd(SCN)_2,2C_9H_7N$ and

$$Cd(SCN)_2,3C_9H_7N,$$

are obtained as yellowish-white, microscopic, prismatic crystals. *Di-* and *tetra-quinoliniumcadmium thiocyanates*, $Cd(C_9H_8N)_2(SCN)_4$ and $Cd(C_9H_8N)_4(SCN)_6$, form transparent, monoclinic crystals, which rapidly become opaque in the air. *Diquinoliniumcadmium bromide*, $Cd(C_9H_8N)_2Br_4,H_2O$, occurs in transparent, colourless, monoclinic crystals; the corresponding *iodide* in yellow crystals. *Quinoline mercuric thiocyanate*, $Hg(SCN)_2,C_9H_7N$, forms colourless crystals; the salts $Hg(C_9H_8N)_2(SCN)_4$; $Hg(C_9H_8N)_4(SCN)_6$; $HgBr_2,2C_9H_8NBr$, and $HgI_2,2C_9H_8NI$ were also prepared; the two former crystallise in glancing, prismatic needles, the *iodide* in yellow, microscopic needles.

Of the *quinoline cobalt* compounds: $Co(SCN)_2,2C_9H_7N,2H_2O$, occurring in well-formed, dark blue, glancing crystals; $Co(C_9H_8N)_2(SCN)_4$; $Co(C_9H_8N)_2Cl_4,2H_2O$; $CoBr_2,2C_9H_7N$, and $Co(C_9H_8N)_2Br_4,2H_2O$ were prepared by the general methods. The chloride occurs in grass-green, tabular crystals, the other three in lustrous, dark blue crystals. The *nickel* compounds, $Ni(SCN)_2,4C_9H_7N$ and $Ni(C_9H_8N)_4(SCN)_6$, occur in green crystals.

Tetraquinoline ferrous thiocyanate, $Fe(SCN)_2,4C_9H_7N$, forms colourless, prismatic needles, which become red in the air; *tetraquinoliniumferrous thiocyanate*, $Fe(C_9H_8N)_4(SCN)_6$, occurs in prismatic, glancing, wine-red crystals, which become dark brown in the air owing to oxidation. The corresponding *manganese* compounds,

$Mn(SCN)_2,4C_9H_7N$,

yellowish-white, well-formed plates, and $Mn(C_9H_7N)_4(SCN)_6$, flesh-coloured, lance-shaped crystals, were prepared. No other quinoline thiocyanate compounds of these three metals could be obtained. The tetraquinolinium compounds of mercury, cadmium, cobalt, nickel, iron, and manganese are isomorphous.

Zinc compounds: $Zn(SCN)_2,2C_9H_7N$ crystallises in microscopic needles; $Zn(C_9H_8N)_2(SCN)_4$ forms milky, prismatic needles. $Zn(C_9H_8N)_2Cl_2$ and the corresponding *bromide* and *iodide* occur in transparent, monoclinic crystals and are isomorphous.

Diquinoline silver thiocyanate, $AgSCN,2C_9H_7N$, forms glistening, milky, regular prisms, which are decomposed by water. No double salt could be obtained. *Diquinoline cuprous thiocyanate*,

$CuSCN,2C_9H_7N$,

crystallises from alcohol in glancing, yellowish-red prisms. The corresponding *chloride* and *bromide* were obtained.

Quinoline thiocyanate, C_9H_8N,SCN, is prepared like the corresponding pyridine compounds, from which it differs in being more stable and in showing greater tendency to crystallise. It occurs in well-formed, clear, monoclinic crystals.

The *aniline* compounds so far obtained contain two molecules of the base, and are characterised by their great stability. $Cd(SCN)_2,2NH_2Ph$ crystallises in prismatic needles. $Cd(NH_3Ph)_2(SCN)_4$ forms colourless, glistening, columnar crystals. $Hg(SCN)_2,2NH_2Ph$ forms colourless, columnar crystals; $Hg(NH_3Ph)_2(SCN)_4$, colourless, lustrous needles. $Co(SCN)_2,2NH_2Ph$ crystallises in prismatic, greyish-violet needles. $Co(NH_3Ph)_2(SCN)_3$ forms lustrous, dark blue, microscopic crystals. $Ni(SCN)_2,2NH_2Ph$ forms clear blue, microscopic needles.

$Ni(NH_3Ph)_2(SCN)_3$

is a clear green, crystalline powder. $Fe(SCN)_2,2NH_2Ph$ forms glistening, yellowish-white needles. $Fe(NH_3Ph)(SCN)_3$ forms red crystals and is comparatively unstable. $Mn(SCN)_2,2NH_2Ph$ crystallises in regular, six-sided, columnar crystals. $Mn(NH_3Ph)_2(SCN)_3$ forms a yellow, crystalline powder. $Zn(SCN)_2,2NH_2Ph$ is obtained in well-formed, glistening, columnar crystals. $Zn(NH_3Ph)_2(SCN)_3$ forms long, glistening, colourless prisms; both salts redden in the air.

Phenylhydrazine Compounds.—$Cd(SCN)_2,5N_2H_3Ph$ forms long, glistening needles. $Cd(SCN)_2,2N_2H_3Ph$ resembles the penta-compound. $Cd(N_2H_4Ph)_4(SCN)_6$ forms colourless, lustrous, microscopic needles. Mercury compounds with phenylhydrazine could not be obtained owing to the reducing action of the latter substance. $Ni(SCN)_2,4N_2H_3Ph$ and $Ni(SCN)_2,6N_2H_3Ph$ both form blue, microscopic crystals, which become dirty-brown on exposure to air. $NiBr_2,6N_2H_3Ph$ resembles the corresponding thiocyanate. $Co(SCN)_2,6N_2H_3Ph$ and $Co(SCN)_2,4N_2H_3Ph$ crystallise in rose-red, microscopic needles which turn brown in the air. $Co(N_2H_4Ph)_4(SCN)_6$ forms green, shining, microscopic needles. $Fe(SCN)_2,6N_2H_3Ph$ crystallises in yellowish-white, well-formed, microscopic needles; the corresponding *bromide* and *iodide* form yellowish-white, microscopic crystals. $Mn(SCN)_2,6N_2H_3Ph$ crystallises in long needles with a silvery lustre and turns brown in the air. $Mn(N_2H_4Ph)_3(SCN)_5$ forms colourless, glistening, microscopic needles. $Zn(SCN)_2,6N_2H_3Ph$ and $Zn(SCN)_2,2N_2H_3Ph$ crystallise in long, prismatic needles. $ZnBr_2,5N_2H_3Ph$ forms slender, colourless crystals.

It is pointed out that there is great analogy between the halogen compounds and those containing the thiocyanate group both as regards the type of compounds formed and the crystallographic relationships.

G. S.

Presence of ψ-Cumene in Roumanian Petroleum. PETRU PONI (*Ann. sci. Univ. Jassy,* 1905, **3**, 217—218).—By the nitration of the fractions boiling between 160—161° and 170—172°, ψ-cumene was detected in the form of its trinitro-derivative, which crystallises in short, quadratic prisms melting at 184—185°. C. S.

Chlorination by means of Sulphuryl Chloride. ALFRED WOHL (D.R.-P. 160102 and 162394. Compare Abstr., 1904, i, 283).—In chlorination by means of sulphuryl chloride, the hydrogen chloride and sulphur dioxide evolved carry with them much sulphuryl chloride, which cannot be recovered completely by cooling. It is, therefore, advisable to pass the vapours through fuming sulphuric acid. The chlorosulphonic acid thus obtained is readily reconverted into sulphuryl chloride. It is still more advantageous to use as absorbing liquid the same compound, such as toluene, as that undergoing chlorination in the principal apparatus, a little acetyl chloride being added to facilitate the reaction. C. H. D.

The Six Isomeric Tribromoxylenes. F. M. JAEGER and JAN J. BLANKSMA (*Proc. K. Akad. Wetensch. Amsterdam,* 1905, **8**, 153—155. Compare Jaeger, Abstr., 1903, i, 240).—The six possible tribromoxylenes have been prepared by the following series of reactions:

On bromination in glacial acetic acid solution, 1 : 2 : 3-xylidine yields 4 : 6-*dibromo*-1 : 2 : 3-*xylidine*, which melts at 56°, and by means of Sandmeyer's reaction is converted into 3 : 4 : 6-*tribromo*-o-*xylene*, melting at 86·5°.

In the same manner, 1 : 2 : 4-xylidine yields 3 : 5-*dibromo*-1 : 2 : 4-*xylidine*, which melts at 63° and is converted into 3 : 4 : 5-*tribromo*-o-*xylene*, melting at 105°.

2 : 4 : 6-*Tribromo*-m-*xylene*, which melts at 85°, is obtained in three ways: (1) by elimination by means of amyl nitrite and copper powder of the amino-group of 2 : 4 : 6-*tribromo*-1 : 3 : 5-*xylidine*, which is obtained by bromination of *s*-xylidine, and melts at 195°. (2) From 4 : 6-dibromo-1 : 3 : 2-xylidine by Sandmeyer's reaction. (3) By Sandmeyer's reaction from 2 : 6-*dibromo*-1 : 3 : 4-*xylidine*, which is formed by hydrolysis of 2 : 6-dibromoaceto-1 : 3 : 4-xylidine and melts at 65°.

4 : 5 : 6-*Tribromo*-m-*xylene*, which melts at 105°, was obtained in two ways: (1) by elimination of the amino-group of 4 : 5 : 6-*tribromo*-1 : 3 : 2-*xylidine*, which is formed by bromination of 4 : 6-dibromo-1 : 3 : 2-xylidine and melts at 190°. (2) By Sandmeyer's reaction from 5 : 6-*dibromo*-1 : 3 : 4-*xylidine*, which is formed by bromination of 6-bromo-1 : 3 : 4-xylidine and melts at 35°.

2 : 4 : 5-*Tribromo*-m-*xylene*, which melts at 87°, was formed by Sandmeyer's reaction from 4 : 5-*dibromo*-1 : 3 : 2-*xylidine*, which is obtained by brominating 4-bromo-1 : 3 : 2-xylidine and melts at 50°.

2 : 3 : 5-*Tribromo*-p-*xylene* is formed from 3 : 5-dibromo-1 : 4 : 2-xylidine and melts at 89°. G. Y.

Chemical Action of Light. X. GIACOMO CIAMICIAN and PAUL SILBER (*Ber.*, 1905, **38**, 3813—3824. Compare Abstr., 1901, i, 36, 329, 390, 547; 1902, i, 433; 1903, i, 39, 171, 562, 626; 1904, i, 161; 1905, i, 335, 414).—Under the influence of light, alcoholic solutions of nitrobenzene yield not only aniline, but a small fraction of a substance soluble in alkali, which is shown to be *p*-aminophenol, proving that the reduction takes place in three stages:

$$C_6H_5{\cdot}NO_2 \rightarrow C_6H_5{\cdot}NH{\cdot}OH \rightarrow C_6H_5{\cdot}NH_2.$$

The basic fraction contains, in addition to aniline, quinaldine, 2-methyl-3-ethylquinoline, or 2-*iso*propyl-3-*iso*butylquinoline, according as ethyl, propyl, or *iso*amyl alcohol is used as solvent. The ethyl-alcoholic solution gives also a *base*, $C_6H_7O_2N$, which crystallises from light petroleum in stout, colourless scales, melts at 70—71°, and reduces Fehling's solution and gold chloride; its *acetyl* derivative, $C_8H_9O_3N$, separates from hot water in large crystals and melts at 178—179°; its *picrate*, $C_{12}H_{10}O_9N_4$, forms yellow needles and melts at 185°, its *benzoyl* derivative, $C_6H_6O_2N{\cdot}COPh$, crystallises from methyl alcohol in rhombic tablets and melts at 192°. The base probably arises from an impurity in the nitrobenzene.

The action of light on a mixture of anisaldehyde and nitrobenzene gives anisic acid, dianisoylphenylhydroxylamine, anisoylanilide, and azoxybenzene and *o*-hydroxyazobenzene (derived from nitrosobenzene).

Dianisoylphenylhydroxylamine,

$$OMe\cdot C_6H_4\cdot CO\cdot NPh\cdot O\cdot CO\cdot C_6H_4\cdot OMe,$$

crystallises from methyl alcohol in colourless prisms melting at 150°.

Experiments were also tried with vanillin, piperonal, salicylaldehyde, and cinnamaldehyde, which yield the corresponding acids, but the ketones, acetone and acetophenone, were found to be without action on the nitrobenzene. T. M. L.

Nitration of *s*-Nitro-*m*-xylene. Jan J. Blanksma (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, **8**, 70—74. Compare Abstr., 1902, i, 442, 600).—The action of a mixture of nitric and sulphuric acids on *s*-nitro-*m*-xylene leads to the formation of 4 : 5 : 6-trinitro-*m*-xylene, together with a smaller quantity of the 2 : 4 : 5-trinitro-compound.

4 : 5 : 6-*Trinitro*-m-*xylene* crystallises from alcohol in long, colourless, monoclinic needles or rods [$a : b : c = 0{\cdot}5950 : 1 : 0{\cdot}2706$; $\beta = 88°11'$], melts at 125°, and, when treated with alcoholic methylamine, is converted into 4 : 6-*dinitromethyl*-1 : 3 : 5-*xylidine*, $C_6HMe_2(NO_2)_2\cdot NHMe$, which melts at 85°, and on bromination yields 2-*bromo*-4 : 6-*dinitromethyl*-1 : 3 : 5-*xylidine*, melting at 146°. On treatment with nitric acid, this forms 4-*bromo*-2 : 6-*dinitro*-3 : 5-*dimethylphenylmethylnitroamine*, $C_6Me_2(NO_2)_2Br\cdot NMe\cdot NO_2$, which melts at 103°.

2 : 4 : 5-*Trinitro*-m-*xylene* separates from alcohol in triclinic crystals [$a : b : c = 2{\cdot}8359 : 1 : 0{\cdot}8510$; $\alpha = 100°54'$, $\beta = 106°59'$, $\gamma = 117°51\frac{1}{2}'$], melts at 90°, and on treatment with alcoholic methylamine is converted into 2 : 4-*dinitromethyl*-1 : 3 : 5-*xylidine*, which melts at 127°, and on bromination yields 6-*bromo*-2 : 4-*dinitromethyl*-1 : 3 : 5-*xylidine*, melting at 175°. This is formed also by the action of alcoholic methylamine on 6-*bromo*-2 : 4 : 5-*trinitro*-m-*xylene*, which melts at 183°, and is obtained by nitrating 6-bromo-5-nitro-*m*-xylene, melting at 56°, or on 5 : 6-*dibromo*-2 : 4-*dinitro*-m-*xylene*, which melts at 193° and is obtained by nitrating 5 : 6-dibromo-*m*-xylene, melting at 11°. 6-*Bromo*-2 : 4-*dinitro*-3 : 5-*dimethylphenylmethylnitroamine*, formed by the action of nitric acid on 6-bromo-2 : 4-dinitromethyl-1 : 3 : 5-xylidine, melts at 152°.

Whilst the action of a mixture of nitric acid of sp. gr. 1·52 and sulphuric acid on 6-bromo- and on 6-chloro-5-nitro-*m*-xylene leads respectively to the formation of 6-*bromo*- and 6-*chloro*-2 : 4 : 5-*trinitro*-m-*xylene*, which melts at 165°, 6-iodo-5-nitro- and 6-iodo-4-nitro-*m*-xylene yield, on nitration, 4 : 5 : 6-trinitro- and 2 : 4 : 6-trinitro-*m*-xylenes, respectively. 6-*Iodo*-5-*nitro*-m-*xylene*, formed by Sandmeyer's reaction from 5-nitro-1 : 3 : 4-xylidine, melts at 165°.

2 : 4 : 6-Trinitro-*m*-xylene separates from a mixture of benzene and alcohol in large, thick, prismatic, bipyramidal, rhombic crystals [$a : b : c = 0{\cdot}6587 : 1 : 0{\cdot}5045$], melts at 182°, and of the three trinitro-*m*-xylenes is the least soluble in alcohol, the most soluble being the 2 : 5 : 6-trinitro-compound melting at 90°.

On treatment with nitric acid of sp. gr. 1·52 at the laboratory temperature, *s*-nitro-*m*-xylene yields 4 : 5-dinitro-*m*-xylene, which, on nitration with a mixture of nitric and sulphuric acids, forms chiefly 4 : 5 : 6-trinitro-*m*-xylene. An attempt to convert this into tetranitro-*m*-xylene by the action of nitric and sulphuric acids at 150°, leads to the formation of a small quantity of an acid oxidation *product*, forming colourless crystals and melting at 190°. G. Y.

Palladium. Alexander Gutbier and A. Krell (*Ber.*, 1905, **38**, 3869—3873. Compare Abstr., 1905, i, 876; ii, 584).—*Palladous methylaniline chloride*, $(NH_2MePhCl)_2,PdCl_2$, crystallises from dilute alcohol in broad, brown needles. The *bromide*, $(NH_2MePhBr)_2,PdBr_2$, crystallises in reddish-brown needles from hydrobromic acid and in plates from dilute alcohol.

Palladous ethylaniline chloride, $(NH_2EtPhCl)_2,PdCl_2$, was obtained in brown needles from hydrochloric acid and in large, brown plates from dilute alcohol. The *bromide*, $(NH_2EtPhBr)_2,PdBr_2$, separates in well-formed brown needles from hydrobromic acid, and in clusters of pyramidal crystals from dilute alcohol.

Palladous diethylaniline chloride, $(NHEt_2PhCl)_2,PdCl_2$, crystallises in dark brown spangles from hydrochloric acid and in dark yellowish-brown needles from dilute alcohol. The corresponding *bromide* forms large, reddish-brown needles and plates.

Diphenyldimethylpalladosammine chloride, $Pd(NHMePh)_2Cl_2$, forms golden-yellow, microcrystalline needles. The *bromide* forms yellowish-red plates.

Diphenyldiethylpalladosammine chloride, $Pd(NHEtPh)_2Cl_2$, is a very sparingly soluble, yellow precipitate. The *bromide* crystallises from much dilute alcohol in dark yellow scales with a green lustre.

T. M. L.

A New Dinitrodiphenylamine. Friedrich Kehrmann and Robert Kaiser (*Ber.*, 1905, **38**, 3778—3779).—2 : 6-Dinitrodiphenylamine, $NHPh\cdot C_6H_3(NO_2)_2$, is formed together with 2 : 4-dinitrodiphenylamine by heating 1-chloro- or 1-iodo-2 : 4-dinitrobenzene, containing small quantities of the 2 : 6-dinitro-isomerides, with aniline. It crystallises in red prisms, melts at 106°, is easily soluble in boiling alcohol or glacial acetic acid, and forms an almost colourless solution in concentrated sulphuric acid. G. Y.

Nitrodiphenylamines. Paul Juillard (*Bull. Soc. chim.*, 1905, [iii], **33**, 1172—1190. Compare Abstr., 1905, i, 843).—Most of the substances described in this paper were prepared for purposes of comparison with the nitration products of Orange IV (anilinobenzeneazobenzene-*p*-sulphonic acid, *loc. cit.*). The following new products were obtained.

2 : 4′-*Dinitrodiphenylnitrosoamine* is prepared by nitrating, under specified conditions, 2-nitrodiphenylnitrosoamine dissolved in acetic acid; it crystallises in colourless leaflets with a faint pink tint, melts and decomposes at 160—162°, is readily soluble in alcohol, less so in acetone, and slightly so in toluene. Boiling alcohol converts it into 2 : 4′-dinitrodiphenylamine (m. p. 217—219°). A mixture of this nitrosoamine with its isomeride, 2 : 2′-dinitrodiphenylnitrosoamine, is produced when the nitration is carried out under certain other conditions; the mixture (molecular combination?) melts and

decomposes into the two corresponding dinitrophenylamines at about 140°.

4 : 4′-*Dinitrodiphenylnitrosoamine* is produced when nitroso-*p*-nitro-orange IV, freshly prepared, is dissolved in dilute nitric acid (33 per cent.) kept at 0°. It crystallises in large, faintly orange-coloured prisms, melts and decomposes at 150°, and is converted by boiling alcohol into 4 : 4′-dinitrodiphenylamine. A mixture of this nitrosoamine with its isomeride, 2 : 4′-dinitrodiphenylnitrosoamine, was obtained by Witt and Nietzke (*Ber.*, 1879, **12**, 1400).

2 : 2′-*Dinitrodiphenylamine* is obtained by heating *o*-nitrodiphenylnitrosoamine, dissolved in acetic acid; it crystallises in golden-yellow laminæ, melts at 166—167°, and is readily soluble in most organic solvents. Nitric acid converts it into 2 : 4 : 2′-trinitrodiphenylamine (m. p. 183—184°), a reaction which may be used for its characterisation.

2 : 4 : 2′-*Trinitrodiphenylamine* may be prepared by heating 2 : 4-dinitrobromobenzene with *o*-nitroaniline at 175° in a closed vessel, or by nitrating 2 : 4′-dinitrodiphenylamine, dissolved in acetic acid, and in other ways; it crystallises from alcohol or acetic acid in heavy yellow prisms, melts at 183—184°, and is slightly soluble in most organic solvents.

2 : 4 : 6 : 2′-*Tetranitrodiphenylamine* may be obtained by heating picryl chloride with *o*-nitroaniline, in presence of alcohol, in a closed vessel or together with 2 : 4 : 2′ : 4′-tetranitrodiphenylamine, by nitrating picrylaniline dissolved in acetic acid. It crystallises in elongated, golden-yellow, prismatic needles, melts at 234°, and is slightly soluble in alcohol, toluene, or acetic acid.

2 : 4 : 6 : 2′ : 4′-*Pentanitrodiphenylamine* is prepared by nitrating picrylaniline, picryl-*p*-nitroaniline, or 2 : 4 : 6-trinitro-orange IV, dissolved in acetic acid. It crystallises from toluene in small, yellow prisms, melts at 193—194°, and dissolves in an aqueous solution of sodium carbonate, from which a *sodium* derivative, crystallising in cruciform bundles of red-coloured rods, is obtained. The *ammonium* derivative, similarly obtained, forms hexagonal crystals. The tinctorial power of this pentanitrodiphenylamine is very slight, and in this respect it differs markedly from the hexanitro-derivative.

In addition to the foregoing new substances, the following were prepared by analogous methods: *o*-nitrodiphenylnitrosoamine, *p*-nitrodiphenylnitrosoamine, *o*-nitrodiphenylamine, 4 : 4′-dinitrodiphenylamine, *op*′-dinitrodiphenylamine (m. p. 217—219°), 2 : 4 : 4′-trinitrodiphenylamine, and 2 : 4 : 2′ : 4′-tetranitrodiphenylamine. In most cases, the solubilities of these substances for a few organic solvents were determined and are given in the original. T. A. H.

Isomeric Schiff's Bases. Otto Anselmino (*Ber.*, 1905, **38**, 3989—3997).—When 6-hydroxy-3-methylbenzaldehyde is mixed with aniline in light petroleum or alcoholic solution, a yellow or a red *anil*, $C_{14}H_{13}ON$, separates, according as the temperature is below or above 32°. The two forms have the same solubility and apparently the same crystalline form; the yellow variety melts at 70°, the red at 74°. The peculiar behaviour observed on heating is dealt with in detail. Both anils give with phenylcarbimide the same *urethane*, $C_{21}H_{18}O_2N_2$, which crystallises from light petroleum in slender, white needles, and melts at 89·5°. They give also the same *hydrochloride*, melting at 205°. Whether the isomerism of the two anils is to be explained by the Hantzsch-Werner hypothesis or whether it is a chemical isomerism due to the presence of quinquevalent nitrogen and quadrivalent oxygen remains to be investigated.

On condensing 6-hydroxy-3-methylbenzaldehyde with *o*-toluidine or with *p*-toluidine, there is no evidence of the existence of the product in more than one form. *6-Hydroxy-3-methylbenzylidene*-o-*toluidine* forms yellow leaflets and melts at 93°. *6-Hydroxy-3-methylbenzylidene*-p-*toluidine* forms yellow needles and melts at 106·5°.

6-Hydroxy-3-methylbenzylidene-p-*chloroaniline*, however, forms yellow, glistening plates, and, when heated, becomes more and more red in colour, melting at 154·5° to an orange-red liquid; on cooling, the change of colour takes place in the reverse direction.

6-Hydroxy-4-methylbenzylideneaniline, obtained from aniline and *m*-homosalicylaldehyde, forms thick, greenish-yellow prisms or slender needles, melts at 93°, and can be transformed into a white, crystalline form by cooling its solutions. The peculiar behaviour of this substance on solidification is described in detail. W. A. D.

Asymmetric Nitrogen. XXI. Activation of Phenylbenzylmethyl*iso*butylammonium Hydroxide. EDGAR WEDEKIND and EMANUEL FRÖHLICH (*Ber.*, 1905, **38**, 3933—3938).—r-*Phenylbenzylmethyl*iso*butylammonium iodide*, $C_{18}H_{24}NI$, is formed by addition of benzyl iodide to methyl*iso*butylaniline, but not of *iso*butyl iodide to benzylmethylaniline. It crystallises in colourless, hexagonal prisms, decomposes at 130—131°, and has solubilities resembling those of phenylbenzylmethylpropylammonium iodide (Abstr., 1905, i, 878). The r-*bromide*, $C_{18}H_{24}NBr$, obtained by mixing molecular amounts of methyl*iso*butylaniline and benzyl bromide, crystallises in microscopic prisms, decomposes at 167°, and is more soluble than the iodide. The d-*camphorsulphonate*, $C_{28}H_{39}O_4NS$, formed from the bromide or iodide and silver *d*-camphorsulphonate in boiling ethyl acetate, crystallises in small rods, melts at 168°, and undergoes little or no resolution when fractionally crystallised from ethyl acetate or methyl formate.

l-*Phenylbenzylmethyl*iso*butylammonium* d-*bromocamphorsulphonate*, $C_{28}H_{38}O_4NSBr$, is prepared from the *r*-bromide and silver *d*-bromocamphorsulphonate in boiling alcoholic ethyl acetate; on concentration of the solution and addition of ether, the salt crystallises in nodular aggregates, melts at about 165°, is very hygroscopic, and is already partly resolved, as it gives $[\alpha]_D + 45°$ and $[M]_D + 256°$. On fractional crystallisation from alcoholic ethyl acetate, the salt yields fractions having $[\alpha]_D + 27·72°$, 13·55°, 3·93°, and −1·55°, and $[M]_D + 156°$, 76·42°, 21·89°, and −8·78°; the last fraction melts at 165°, and, when treated with potassium iodide in concentrated aqueous solution, forms l-*phenylbenzylmethyl*iso*butylammonium iodide*, which decomposes at 130—131°, and in absolute alcoholic solution has $[\alpha]_D - 91·59°$ and $[M]_D - 349°$ at 25°, or in chloroform $[\alpha]_D - 78·29°$ and $[M]_D - 298°$. The diminished rotation in chloroform solution is due to racemisation, as after one hour it becomes $[\alpha]_D - 66·26°$. G. Y.

Absence of Isomerism in Substituted Ammonium Compounds. HUMPHREY O. JONES (*Proc. Camb. Phil. Soc.*, 1905, **13**, 169).—The only stable isomerides of quinquevalent nitrogen compounds are the α- and β-phenylbenzylmethylallylammonium compounds described by Wedekind (Abstr., 1900, i, 155). The author finds that the β-compound is really phenylbenzyldimethylammonium iodide (Trans., 1903, **83**, 1409); an abnormal reaction, therefore, occurs between benzylallylaniline and methyl iodide, in which the allyl iodide is removed. L. M. J.

Derivatives of Phenylcarbamic Acid. F. M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, **8**, 127—136. Romburgh, Abstr., 1901, i, 201).—The following derivatives of phenylcarbamic acid have been examined crystallographically.

Methyl phenylcarbamate is rhombic [$a:b:c = 1·5952:1:?$], and has the sp. gr. 1·251 at 19°. Methyl phenylmethylcarbamate is rhombic [$a:b:c = 0·8406:1:0·3320$], and has the sp. gr. 1·296 at 19°. Methyl 4-nitrophenylmethylcarbamate separates from alcohol or benzene in small, delicate needles or flat, monoclinic crystals [$a:b:c = 0·6640:1:?$; $\beta = 70°58'$], and has the sp. gr. 1·522 at 14°. Methyl 2:4-dinitrophenylmethylcarbamate is monoclinic [$a:b:c = 0·7597:1:1·0875$; $\beta = 88°43\frac{1}{3}'$], and has the sp. gr. 1·506 at 14°. Methyl 2:4:6-trinitrophenylmethylcarbamate occurs in two modifications: the α-modification, which crystallises from alcohol, acetone, or benzene, is monoclinic [$a:b:c = 0·5758:1:0·8382$; $\beta = 75°41'$], melts at 118°, has the sp. gr. 1·612 at 19°, and slowly changes into the β-modification, which is deposited sometimes together with the α-modification from alcohol in long, rhombic needles [$a:b:c = 0·6596:1:?$]; it melts at 114—118° and has the sp. gr. 1·601 at 19°. Ethyl 2:4-dinitrophenylmethylcarbamate separates from a mixture of benzene and light petroleum in large, colourless, lustrous, monoclinic crystals [$a:b:c = 0·6525:1:0·7035$; $\beta = 69°59'$], and has the sp. gr. 1·461 at 19°. Ethyl 2:4:6-trinitrophenylmethylcarbamate crystallises from a mixture of benzene and light petroleum in delicate, flat, sherry-coloured, monoclinic needles [$a:b:c = 0·9759:1:0·3929$; $\beta = 67°7'$], and has the sp. gr. 1·471 at 14°.

2:4:6-*Trinitrophenylmethylnitroamine*, $C_6H_2(NO_2)_3·NMe·NO_2$, formed by the action of fuming nitric acid on 2:4-dinitromethylaniline, melting at 178°, crystallises from a mixture of acetone and benzene in small, strongly-refracting, monoclinic needles [$a:b:c = 2·7823:1:3·5242$; $\beta = 73°31\frac{1}{2}'$], melts at 127°, and has the sp. gr. 1·570 at 19°. G. Y.

Constitution of Aromatic Purpuric Acids. VIII. Picramic Acid and Potassium Cyanide. WALTHER BORSCHE and ARNOLD HEYDE (*Ber.*, 1905, **38**, 3938—3942. Compare Abstr., 1900, i, 645; 1902, i, 226; 1904, i, 166, 574; 1905, i, 51, 894).—Picramic acid (2:4-dinitro-6-aminophenol) interacts with potassium cyanide less easily than do the 2:4-dinitrophenols investigated previously, with formation of the potassium derivatives of 2:4-dinitro-6-amino-3-cyanophenol and of 4-nitro-2-amino-6-hydroxylamino-5-cyanophenol in about equal amounts.

Potassium picramopurpurate (*potassium 4-nitro-2-amino-6-hydroxylamino-5-cyanophenoxide*), $C_7H_5O_4N_4K,H_2O$, forms an almost black, crystalline powder, having a green, metallic lustre, and when treated with phosphoric acid yields the *phenol* as an unstable, dark brown, flocculent precipitate. The *ammonium* salt, $C_7H_5O_4N_4\cdot NH_4$, prepared by the action of a current of carbon dioxide on the aqueous solution of the potassium salt, covered with ether, and treatment of the dry ethereal solution with ammonia, forms a red, flocculent precipitate.

Potassium 2 : 4-*dinitro-6-amino-3-cyanophenoxide*, $C_7H_3O_5N_4K$, separates from water or aqueous potassium cyanide solution in dark brown crystals with metallic lustre, decomposes with evolution of nitric oxide when heated, and dissolves in water to form a red solution. The *phenol*, $C_7H_4O_5N_4$, liberated from the potassium salt by an excess of dilute hydrochloric acid, separates from methyl alcohol as a reddish-yellow powder and detonates when heated. The *ammonium* salt forms dark red crystals and decomposes explosively at 150°. When boiled with sodium nitrite and sulphuric acid in aqueous alcoholic solution, 2 : 4-dinitro 6-amino-3-cyanophenol yields 3-hydroxy-2 : 6-dinitrobenzonitrile.

G. Y.

Nitrohalogen Derivatives of Anisole. Frédéric Reverdin and Karl Philipp (*Ber.*, 1905, **38**, 3774—3777. Compare Reverdin and Eckhard, Abstr., 1900, i, 28).—2-*Chloro*-4 : 6-*dinitroanisole*, formed by the action of nitric acid of sp. gr. 1·52 and concentrated sulphuric acid on *o*-chloro-*p*-nitroanisole, when reduced with tin and hydrochloric acid, yields the m-*diamine*, which condenses with chlorodinitrobenzene in alcoholic sodium acetate solution to form a carmine or yellowish-red, crystalline *substance*, melting at 182—185°.

Nitration of 2-chloro-5-nitroanisole at 19—37° leads to the formation of 2-*chloro*-4 : 5-(or 5 : 6)*dinitroanisole*, which crystallises in colourless needles, melts at 79°, is easily soluble in the ordinary organic solvents, and, when reduced, yields a substance which gives the *o*-diamine reaction with benzaldehyde and phenanthraquinone.

The action of nitric acid of sp. gr. 1·52 and concentrated sulphuric acid on *m*-chloroanisole at −10° to +20° leads to the formation of m-*chlorodinitroanisole*, $C_7H_5O_5N_2Cl$, which crystallises in leaflets and melts at 102—104°, whilst the action of nitric acid alone leads to the formation of a *nitro*- or *dinitro*-derivative, which crystallises in white needles and melts at 81°.

When nitrated in concentrated sulphuric acid solution at −10°, *m*-iodoanisole yields m-*iododinitroanisole*, which melts at 102°.

G. Y.

Decahydro-α-naphthol and Δ-Octahydronaphthalene. Henri Leroux (*Compt. rend.*, 1905, **141**, 953—954. Compare Abstr., 1905, i. 278).—Decahydro-*α*-naphthol, obtained by the direct hydrogenation of *α*-naphthol below 200° by Sabatier and Senderens' method, crystallises from light petroleum or acetone in colourless needles melting at 62°, boils at 109° under 12 mm. or at 230° under the ordinary pressure, is sparingly soluble in water, readily so in the ordinary solvents, and is volatile in steam. The *acetate*, $C_{10}H_{17}\cdot OAc$, is a colourless liquid with an agreeable fruity odour, boiling at 127° under 18 mm. pressure; the *benzoate*, $C_{10}H_{17}OBz$, obtained by heating decahydro-α-naphthol with benzoic anhydride in a sealed tube at 175° for twelve hours, crystallises from alcohol in colourless plates melting at 68° and is readily soluble in ether or benzene. The *phenylcarbamate*,

$$NHPh\cdot CO\cdot OC_{10}H_{17},$$

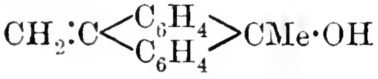
crystallises from alcohol in thin needles melting at 110°.

A-*Octahydronaphthalene*, $C_{10}H_{16}$, obtained by heating decahydro-α-naphthol with phosphoric oxide, anhydrous oxalic oxide, or potassium hydrogen sulphate, differs in the nature of its derivatives from the corresponding compound obtained from decahydro-β-naphthol, which should be designated *B*-octahydronaphthalene (compare Abstr., 1905, i, 278). *A*-Octahydronaphthalene is a colourless liquid boiling at 190—191°, having a sp. gr. 0·931 at 0° or 0·914 at 17°, and n_D 1·4993 at 17°; it unites directly with bromine to form A-*dibromo-octahydronaphthalene*, $C_{10}H_{16}Br_2$, which crystallises from chloroform in colourless prisms, begins to sublime at 120°, and melts at 145°. M. A. W.

γ-Substituted Anthracene Derivatives. Parts II and III.

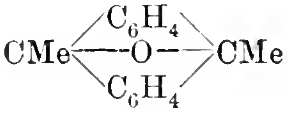
Alfred Guyot and Ch. Staehling (*Bull. Soc. chim.*, 1905, [iii], 33, 1144—1152, 1152—1161. Compare Abstr., 1905, i, 885).—9 : 10-*Dihydroxy*-9 : 10-*dimethyldihydroanthracene*, $C_6H_4{<}\begin{matrix}CMe(OH)\\ CMe(OH)\end{matrix}{>}C_6H_4$, obtained by the interaction of magnesium methyl iodide with anthraquinone, crystallises from methyl alcohol in large, colourless, transparent prisms, effloresces in air, but retains 1 mol. of the solvent even when dried at 100° under reduced pressure, melts when anhydrous at 181°, and dissolves in sulphuric acid to form a green solution, which slowly becomes yellow. The *dimethyl ether*, prepared by the addition of a small quantity of hydrochloric acid to a solution of the dihydroxy-compound in methyl alcohol, crystallises in needles, melts at 197°, and gives a green coloration with sulphuric acid.

When 9 : 10-dihydroxy-9 : 10-dimethyldihydroanthracene, dissolved in acetic acid, is boiled, there is formed a bright yellow, crystalline powder, which melts at about 223° and is slightly soluble in organic solvents. The constitution of this *substance* is considered to be represented by one of the following formulæ, of which (I) is regarded as the more probable:



$$CH_2{:}C{<}\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}{>}CMe\cdot OH$$

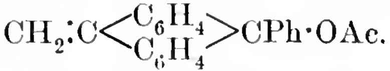
(I.)



(II.)

The *methyl ether* of this dehydration product is formed when the dimethyl ether of 9 : 10-dihydroxy-9 : 10-dimethyldihydroanthracene is heated at 100°. It crystallises from a mixture of benzene and methyl alcohol in long, pale straw-coloured needles and is readily soluble in benzene or its homologues, less so in alcohols. When to the dihydroxy-compound, dissolved in acetic acid, a few drops of hydrochloric or sulphuric acid are added, a second dehydration *product* is also formed: this is a yellow. crystalline powder, which melts above 330°, is almost insoluble in organic solvents, and is consequently difficult to purify. Its composition is represented by the formula $C_{36}H_{74}O$.

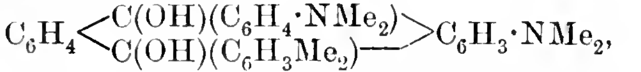
10-*Hydroxy-9-methoxy-9-phenyl-*10-*methyldihydroanthracene,* obtained by the action of magnesium methyl iodide on the methyl ether of phenyloxanthranol, crystallises from a mixture of alcohol and benzene in silky, white needles and melts at about 201°. The corresponding *ethoxy-*derivative forms colourless crystals and melts at 176°. Each of these ethers gives a green coloration with sulphuric acid and, when dissolved in acetic acid and boiled for a few minutes, furnishes the dehydration product 9-*acetoxy*-9-*phenyl*-10-*methylenedihydroanthracene,*



$$CH_2{:}C\left<\begin{array}{c}C_6H_4\\C_6H_4\end{array}\right>CPh{\cdot}OAc.$$

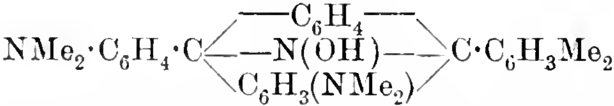
This is a yellow, crystalline substance showing a green fluorescence; it melts at 221°, and when hydrolysed with hydrochloric acid yields 9 : 10-*dihydroxy*-9-*phenyl*-10-*methyldihydroanthracene,* which forms brilliant yellow crystals melting at 132°. On oxidation with potassium dichromate in acetic acid, the acetyl derivative yields phenyloxanthranol and some 9 : 10-dihydroxy-9-phenyl-10-methyldihydroanthracene.

3-*Dimethylamino*-9 : 10-*dihydroxy*-9-p-*dimethylaminophenyl*-10-mp-*dimethylphenyldihydroanthracene,*



$$C_6H_4\left<\begin{array}{l}C(OH)(C_6H_4{\cdot}NMe_2)\\C(OH)(C_6H_3Me_2)\end{array}\right>C_6H_3{\cdot}NMe_2,$$

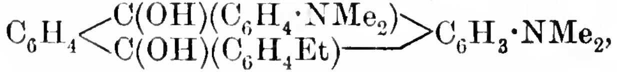
obtained by the condensation of tetramethyldiaminophenyloxanthranol with *o*-xylene in presence of sulphuric acid, is a colourless, crystalline powder, melts at 185°, and is readily soluble in benzene or its homologues. Its *salts* with mineral acids are reddish-brown and dye wool and cotton, mordanted with tannin and tartar emetic, in yellowish-brown tints. It condenses with hydroxylamine to form a *compound,* which, by analogy with those similarly obtained by Haller and Guyot from phthalyl-green and its homologues, has the constitution



$$NMe_2{\cdot}C_6H_4{\cdot}C\left<\begin{array}{c}C_6H_4\\N(OH)\\C_6H_3(NMe_2)\end{array}\right>C{\cdot}C_6H_3Me_2.$$

This forms small, white crystals and melts at 246°. With phenylhydrazine, an analogous *product* is formed which is crystalline and melts at 236°.

3-*Dimethylamino*-9 : 10-*dihydroxy*-9-p-*methylaminophenyl*-10-p-*ethylphenyldihydroanthracene,*



$$C_6H_4\left<\begin{array}{l}C(OH)(C_6H_4{\cdot}NMe_2)\\C(OH)(C_6H_4Et)\end{array}\right>C_6H_3{\cdot}NMe_2,$$

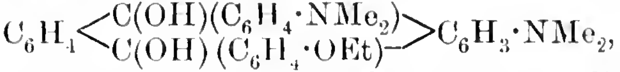
produced by condensing ethylbenzene with tetramethyldiaminophenyloxanthranol, is a colourless, crystalline powder and melts at 163°. The *condensation product* with hydroxylamine, $C_{32}H_{33}ON_3$, forms colourless crystals and melts at 221°; that with phenylhydrazine, $C_{38}H_{38}N_4$, is yellowish-brown and crystalline and melts at 215°.

3-*Dimethylamino*-9 : 10-*dihydroxy*-9-p-*dimethylaminophenyl*-10-p-*methoxyphenyldihydroanthracene,* similarly obtained from anisole and tetramethyldiaminophenyloxanthranol and purified by means of its *zincochloride,* forms small, white crystals and melts at 176°. The hydroxylamine *condensation product* forms small, white crystals and melts at 203°; that with phenylhydrazine forms brilliant yellow crystals containing 1 mol. of the solvent (benzene) and melts at 213°. When a solution of the original base in hydrochloric acid is treated with zinc dust until it is just decolorised, the *leuco-base*,

$$C_6H_4{<}\begin{matrix}CH(C_6H_4\cdot NMe_2)-\\ C(OH)(C_6H_4\cdot OMe)\end{matrix}{>}C_6H_3\cdot NMe_2,$$

is formed; this crystallises from a mixture of benzene and alcohol in small, colourless crystals, melts at 246°, and dissolves in acids without producing any coloration.

3-*Dimethylamino*-9 : 10-*dihydroxy*-9-p-*dimethylaminophenyl*-10-p-*ethoxyphenyl*-9 : 10-*dihydroanthracene*,



$$C_6H_4{<}\begin{matrix}C(OH)(C_6H_4\cdot NMe_2)\\ C(OH)(C_6H_4\cdot OEt)-\end{matrix}{>}C_6H_3\cdot NMe_2,$$

obtained by condensing phenetole with tetramethyldiaminophenyloxanthranol and purified by means of the crystalline *zincochloride*, is a colourless, crystalline powder and melts at 175°. Its *condensation product* with hydroxylamine crystallises from benzene in colourless needles and melts at about 208°; that with phenylhydrazine forms brilliant yellow needles and melts at about 186°.

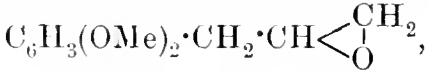
Phenol condenses with tetramethyldiaminophenyloxanthranol to form a dihydroxy-derivative of the usual type, which yields a crystalline red zincochloride. The base was, however, not obtained pure. The condensation product with pyrogallol yields a *sulphate*, which occurs in carmine-red needles and dyes cotton mordanted with alumina an intense indigo-blue, sensitive to acids and to light. The analogous *product* obtained with catechol behaves similarly, yielding a greener, still more fugitive, blue. In neither of these cases was the free base obtained pure.
T. A. H.

1 : 3 : 6-Trihydroxynaphthalene. RICHARD MEYER and ERNST HARTMANN (*Ber.*, 1905, **38**, 3945—3956. Compare Kalle & Co., D.R.-P. 112176, 1899).—1 : 3 : 6-Trihydroxynaphthalene is best prepared on the small scale by fusing sodium 1 : 6-dihydroxynaphthalene-3-sulphonate with three and a third times its weight of sodium hydroxide added in the form of a concentrated solution. After some three hours at 250°, the reaction is complete, and, on the addition of concentrated hydrochloric acid, the crystalline *hydrochloride*, $C_{10}H_5(OH)_3,HCl(?)$, is obtained in the form of yellow, well-developed needles. The pure hydroxy-derivative is most readily obtained by decomposing the hydrochloride with water; it may be crystallised from hot water if the solution is rapidly cooled, and forms doubly-refracting, cube-shaped crystals, melts at 95°, and is sparingly soluble in benzene, toluene, chloroform, or light petroleum. With ferric chloride, it gives a yellowish-brown precipitate. The *triacetate*, $C_{10}H_5(OAc)_3$, crystallises in colourless needles, melts at 112—113°, and is insoluble in alkalis. The *tribenzoate*, $C_{10}H_5(O\cdot COPh)_3$, crystallises from acetone.

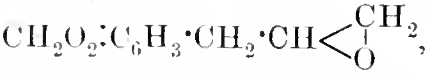
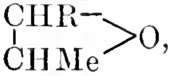
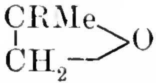
A *polymeride*, $C_{20}H_{16}O_6$, probably 2 : 4 : 7 : 3′ : 6′ : 8′-*hexahydroxy*-1 : 2-*dihydro*-2 : 2′-*dinaphthyl*, $C_{10}H_6(OH)_3\cdot C_{10}H_4(OH)_3$, is obtained when an aqueous solution of the trihydroxynaphthalene is boiled for some time, especially in presence of animal charcoal. It crystallises in colourless plates, does not melt, but decomposes at about 304°, and dissolves readily in alcohol, ether, or acetone. The solution in sodium hydroxide is yellow, turns red only after several days, and even then is not fluorescent. With ferric chloride, it gives a reddish-brown precipitate. The *acetate*, $C_{20}H_{10}(OAc)_6$, crystallises from water in colourless plates and melts at 200°. The *benzoate*, $C_{20}H_{10}(O{\cdot}COPh)_3$, forms colourless needles melting at 244°.

*Benzeneazo-*1 : 3 : 6-*trihydroxynaphthalene*, $C_{10}H_4(OH)_3{\cdot}N_2Ph$, forms indistinct, microscopic, red needles which dissolve readily in most organic solvents. The polymeride also yields an azo-dye, but this could not be obtained in a crystalline form. No definite products have been obtained by distilling the polymeride with zinc dust. J. J. S.

Some Aromatic Ethylene Oxides. ERNEST FOURNEAU and MARC TIFFENEAU (*Compt. rend.*, 1905, **141**, 662—663. Compare Abstr., 1905, i, 523, 591).—In addition to the aromatic monosubstituted ethylene oxides already described, namely, allylbenzene oxide and estragole oxide (the latter boils at 258—263° and not at 153—156° as stated in the original paper), *methyleugenole oxide*,

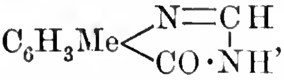


$$\mathrm{C_6H_3(OMe)_2{\cdot}CH_2{\cdot}CH}<\begin{array}{l}\mathrm{CH_2}\\ \mid\\ \mathrm{O}\end{array},$$

boiling at 165—170° under 15 mm. pressure, and *safrole oxide*,  $\mathrm{CH_2O_2{:}C_6H_3{\cdot}CH_2{\cdot}CH}<\begin{array}{l}\mathrm{CH_2}\\ \mid\\ \mathrm{O}\end{array}$, boiling at 160—165° under 15 mm. pressure, have been prepared. These oxides are partially decomposed on heating into the isomeric aldehydes, dihydrocinnamaldehyde, *p*-methoxydihydrocinnamaldehyde, dimethoxydihydrocinnamaldehyde, and methylenedioxydihydrocinnamaldehyde respectively. Symmetrical disubstituted ethylene oxides of the type  $\begin{array}{l}\mathrm{CHR}-\\ \mid\\ \mathrm{CHMe}\end{array}>\mathrm{O}$, where R represents an aromatic radicle, are converted into the isomeric ketones on distillation, thus methyl*iso*eugenole oxide yields dimethoxyphenylacetone (compare Höring, Abstr., 1905, i, 592). Asymmetrical disubstituted ethylene oxides of the type  $\begin{array}{l}\mathrm{CRMe}\\ \mid\\ \mathrm{CH_2}-\end{array}>\mathrm{O}$ are readily converted by heating into the corresponding aldehyde, $CHRMe{\cdot}CHO$ (compare Behal and Tiffeneau, Abstr., 1905, i, 883). M. A. W.

Presence of Lupeol in some kinds of Gutta-percha. PIETER VAN ROMBURGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, **8**, 137).—The alcohol melting at 210°, obtained on hydrolysis of Tschirch's crystalalban (Abstr., 1904, i, 76, 905), is identical with lupeol (Schulze, Abstr., 1904, i, 582). It is obtained in the form of its acetate from djelutung, the product of the milky juice of some species of *Dyera*, which is related to gutta-percha and is known commercially as bresk or pontianak. On oxidation with chromic acid, it yields a crystalline *ketone* which melts at 169° and forms a crystalline *product* with hydroxylamine.

Djelutung yields also an acetic ester which melts at 238°; this has been isolated previously from the gutta-percha of *Payena Leerii*, and on hydrolysis yields an *alcohol* melting at 195°. G. Y.

Nitro-*m*-toluic Acids. Waldemar Findeklee (*Ber.*, 1905, **38**, 3553—3558).—Contrary to the statement in *Beilstein's Handbuch* that 4-nitro-*m*-toluic acid melts at 219° and yields an amino-acid melting at 172°, the author shows that the acid possessing these constants is the 2-nitro-acid, whilst the 4-acid melts at 134° and yields an amino-acid melting at 175°. The 4-nitro-acid yields a white, insoluble silver salt; the *amide*, $NO_2\cdot C_6H_3Me\cdot CO\cdot NH_2$ [4 : 1 : 3], separates from alcohol in stout, flat needles and melts at 176—177°. The 4-amino-acid yields an amide, $NH_2\cdot C_6H_3Me\cdot CO\cdot NH_2$ [4 : 1 : 3], melting at 179°. The 2-amino-acid, which is formed as a by-product in the action of nitric acid on *m*-toluic acid, condenses with formamide to form 8-*methylquinazolone*,  $C_6H_3Me{<}\begin{matrix}N{=}CH\\ |\\ CO\cdot NH\end{matrix}$, which separates from alcohol in needles, melts at 251°, and gives a crystalline *platinichloride* and *chromate*. T. M. L.

Cinnamic Acid from Storax. Emil Erlenmeyer, jun. (*Ber.*, 1905, **38**, 3891—3892. Compare Abstr., 1905, i, 892).—Cinnamic acid from storax gave a quantitative yield of the brucine salt melting at 135°, and no trace of the salt of lower melting point. In 1 per cent. solution, the salt gave no rotation, but showed a dextro-rotation in a 5 per cent. solution. It is suggested that the synthetical acid contains a racemic modification, produced during saponification with sodium hydroxide. T. M. L.

Syntheses of Carboxylic Acids. II. Josef Houben (*Ber.*, 1905, **38**, 3796—3801. Compare Abstr., 1903, i, 825; Houben and Kesselkaul, Abstr., 1903, i, 42).—On addition of traces of methyl iodide to a mixture of 1 mol. of dibromobenzene and 1 mol. of powdered magnesium in ethereal solution, a violent reaction takes place, which must be moderated by cooling with ice and concentrated sulphuric acid; the action of anhydrous carbon dioxide on the product and subsequent decomposition with ice and dilute hydrochloric acid leads to the formation of small quantities of *p*-bromobenzoic and terephthalic acids, together with traces of 4 : 4′-dibromoacetophenone (compare Bodroux, Abstr., 1904, i, 64; Jocitsch, *Chem. Zeit.*, 1903, **27**, 56).

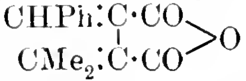
4-*Bromo-α-naphthoic acid*, obtained in the same manner from 1 : 4-dibromonaphthalene in a yield of 20 per cent. of the theoretical, sublimes in small, colourless, glistening crystals and melts at 204—209°. It could not be obtained in a state of purity.

Dihydropinenecarboxylic acid, formed from pinene hydrochloride (Houben and Kesselkaul, *loc. cit.*), crystallises in prisms, melts at 72—74°, and boils at 153° under 13 mm. or at 268° under the atmospheric pressure. The *sodium* salt forms colourless leaflets; the *silver* salt is obtained as a white precipitate, sensitive to light. The *anhydride*, $C_{22}H_{34}O_3$, formed by boiling the acid with acetyl chloride, crystallises from alcohol in glistening, silky threads and melts at 211—212°. Together with the carboxylic acid, pinene hydrochloride yields borneol, and Étard and Meker's dicamphene hydride.

The action of magnesium and carbon dioxide on bornyl chloride leads to the formation of an acid which melts at 72° (compare Zelinsky, Abstr., 1903, i, 185). G. Y.

Acid Function of Aromatic Hydroxyl. Alfred Thiel, A. Schumacher, and Hermann Roemer (*Ber.*, 1905, **38**, 3860—3862).—The basicity of aromatic hydroxylic compounds can be determined even more effectively by conductivity measurements than by titration with sensitive indicators. Using this method, it is found that orcylaldehyde is dibasic and gives coloured alkaline solutions; orsellic acid behaves similarly, but paraorsellic acid (orcincarboxylic acid) is monobasic and yields colourless alkali salts. This result is in accord with the view that in the latter compound both hydroxyls are in ortho-positions relatively to the carboxyl, whilst in the former acid only one hydroxyl is in the ortho-position to the carboxyl group.

T. M. L.

Butadiene Compounds. IX. Yellow Monoarylfulgides. Hans Stobbe (*Ber.*, 1905, **38**, 3893—3897. Compare Abstr., 1905, i, 857).—[With Alfred Lenzner.]—*δ-Phenyl-αα-dimethylfulgenic acid*, $CMe_2\!:\!C(CO_2H)\cdot C(CO_2H)\!:\!CHPh$, prepared from benzaldehyde and ethylteraconate, crystallises from 80 per cent. acetic acid in irregular, colourless prisms and softens and melts at 213—214°, decomposing and becoming yellow. Acetyl chloride converts it into a yellow and a white *fulgide*,  $\left.\begin{array}{l}\mathrm{CHPh\!:\!C\cdot CO}\\ \mathrm{CMe_2\!:\!C\cdot CO}\end{array}\right>\mathrm{O}$; both melt at 115—116° and crystallise in rhombohedra; in sunlight, the yellow form becomes lighter, the white form becomes yellow, and when recrystallised both forms again separate. From a supersaturated solution of the yellow form, a yellow crystal brings down only the yellow form, a white crystal a mixture; so, conversely, with the white form.

[With Emil Wahl.]—*δ-p-Tolyl αα-dimethylfulgenic acid*,

$$CMe_2\!:\!C(CO_2H)\cdot C(CO_2H)\!:\!CH\cdot C_6H_4Me,$$

prepared from *p*-tolualdehyde and ethyl dimethylitaconate, crystallises from 50 per cent. acetic acid and melts at 224°. The *fulgide*, $C_{15}H_{14}O_3$, crystallises from light petroleum in pointed, yellow prisms and melts at 107°.

T. M. L.

Butadiene-compounds. X. Two Cumyldimethylfulgenic Acids and a Third Isomeride. Hans Stobbe and Karl Leuner (*Ber.* 1905, **38**, 3897—3903).—Two stereoisomeric fulgenic acids are produced by the condensation of cuminaldehyde with ethyl tetraconate.

δ-Cumyl-αα-dimethylfulgenic acid,

$$CHMe_2\cdot C_6H_4\cdot CH\!:\!C(CO_2H)\cdot C(CO_2H)\!:\!CMe_2,$$

the main product, separates from 80 per cent. acetic acid in microscopic crystals, softens at 215°, and melts at 225°, liberating gas and becoming yellow. The *barium* salt, $C_{17}H_{18}O_4Ba,2H_2O$, forms a flocculent precipitate, loses H_2O at 150° and the second molecule at 170°. The *fulgide*, $C_{17}H_{18}O_3$, of normal molecular weight, crystallises from light petroleum in yellow, sharp-edged forms of the colour of monoclinic sulphur and melts at 85°. When a solution in benzene containing iodine is exposed to light, it is for the most part converted into the stereoisomeride.

The *allo*-acid crystallises from dilute acetic acid in small, six-sided tablets, begins to melt at 200°, and decomposes vigorously at 208°.

The *allo*-fulgide separates from light petroleum in long prisms and melts at 112°.

Both acids are reduced by sodium amalgam to a *dihydro*-acid, $C_{17}H_{22}O_4$, which melts at 135—137°. This and the two preceding acids, when oxidised, yield cuminaldehyde, acetone, and oxalic acid.

A third acid found in the interaction was shown to be *α-cumylidene-δδ-dimethylparaconic acid,*  $C_3H_7\cdot C_6H_4\cdot CH{:}C\!<\!\begin{matrix}CH(CO_2H)\\ CO\text{———}O\end{matrix}\!>\!CMe_2$; the acid softens and melts at 192° without decomposing. T. M. L.

Hydroxydiphenic Acids. Julius Schmidt and Richard Schall (*Ber.*, 1905, **38**, 3769—3774).—4-Amino- and 4 : 4′-diamino-diphenic acids may be readily diazotised, and when the solutions of the diazonium salts are heated, the corresponding hydroxy-acids are obtained. 4-*Hydroxydiphenic acid* crystallises in yellow prisms, melts at 245—246°, dissolves readily in alcohol, ether, or water, but only sparingly in benzene. 4 : 4′-*Dihydroxydiphenic acid,* $C_{14}H_{10}O_6,H_2O$, crystallises in pale yellow prisms, melting and decomposing at 272—273°. *Silver* and *barium* salts have been prepared. The *diacetyl* derivative, $C_{12}H_6(OAc)_2(CO_2H)_2$, crystallises in colourless needles and melts and decomposes at 222—223°.

When 6 : 6′-diaminodiphenic acid is diazotised and the solution heated, 6-*amino*-6′-*hydroxydiphenic acid,* $NH_2\cdot C_{12}H_6(CO_2H)_2\cdot OH$, is produced. It forms yellow, microscopic needles which melt and decompose at 312—313°. It dissolves only sparingly in the usual organic solvents. The formation of an aminohydroxy- and not of a dihydroxy-acid is attributed to stereochemical causes.

The acids are not esterified by the usual catalytic methods. Full directions for the preparation of the two diamino-acids are given (compare Schmidt and Kämpf, Abstr., 1904, i, 70 and 71). J. J. S.

Constitution of Fluorescein. Emilio Noelting (*Ber.*, 1905, **38**, 4023).—The author in a recent paper (Abstr., 1905, i, 935) had overlooked the work of R. Meyer (Abstr., 1895, i, 291, 538; 1897, i, 69).
W. A. D.

Mutual Exchange of Aromatic Complexes. Richard Meyer and Hermann Pfotenhauer (*Ber.*, 1905, **38**, 3958—3963).—Fluorescein is formed when phenolphthalein and resorcinol are heated in an oil-bath at 180—200° during some forty-eight hours. The reaction is not complete even when a large excess of resorcinol is used. The fluorescein was characterised by conversion into eosin.

Catecholphthalein is completely transformed into fluorescein when heated at 210—220° with five times its weight of resorcinol. Quinolphthalein is not decomposed when heated with resorcinol and fluorescein is not decomposed when heated with phenol. J. J. S.

Thio-compounds prepared from Ketones and Aldehydes. Compagnie Morana (D.R.-P. 162059).—Ketones and aldehydes react with aqueous solutions of alkali sulphides or polysulphides, the ketonic oxygen being replaced by sulphur, and condensation of the aldehyde group taking place at the same time, water being eliminated. Thus, acetophenone and formaldehyde yield a *compound*, C_9H_8S [? $CH_2:CH\cdot CSPh$], which separates as a viscous, yellow oil and boils with partial decomposition at 130—140° under 20 mm. pressure. It is insoluble in water, ether, or light petroleum, sparingly soluble in alcohol, readily so in benzene, and does not distil in a current of steam.

Benzophenone, formaldehyde, and alkali sulphides yield a *compound*, $C_{13}H_{10}S$, which crystallises in white needles, melts at 36°, and dissolves readily in alcohol. Acetone and citral yield a *compound*, $C_{13}H_{20}S$, which forms a yellow oil with a faint odour of leeks, and boils at 150—153° under 12 mm. pressure. C. H. D.

Benzylidene Derivatives of Anthrone or Anthranol.

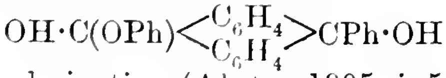
ALBIN HALLER and PADOVA (*Compt. rend.*, 1905, **141**, 857—861).—Liebermann's anthranol, $C_6H_4<\begin{matrix}C(OH)\\ |\\ CH\text{——}\end{matrix}>C_6H_4$ (compare Abstr., 1882, 855; 1887, 965), reacts in alkaline medium as its tautomeride, anthrone, $CO<\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}>CH_2$ (compare Goldmann, Abstr., 1888, 714, 1202; Thörner and Zincke, Abstr., 1878, 231), condensing with aromatic aldehydes to form compounds of the type $CO<\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}>C:CHR$. Benzylideneanthrone, $CO<\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}>C:CHPh$, prepared by heating anthranol and benzaldehyde in pyridine solution containing a little piperidine, forms yellow needles melting at 126—127° (compare Levi, Abstr., 1885, 1240; Bach, Abstr., 1890, 1144, 1425), and can also be prepared by dehydrating, by means of hydrogen chloride, benzyloxanthranol, $CO<\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}>C(CH_2Ph)\cdot OH$, obtained from anthraquinone and magnesium benzyl chloride (compare Haller and Guyot, Abstr., 1904, i, 314). *Anisylideneanthrone* (p-*methoxybenzylideneanthrone*), $CO<\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}>C:CH\cdot C_6H_4\cdot OMe$, crystallises from alcohol or acetic acid in long, yellow needles, melting at 140·5—141·5°, and is less soluble in alcohol, acetic acid, ethyl acetate, chloroform, or benzene than the benzylidene compound. m-*Nitrobenzylideneanthrone*,

$$CO<\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}>C:CH\cdot C_6H_4\cdot NO_2,$$

melts at 165·5—166·5°, is readily soluble in chloroform, benzene, acetic acid, or pyridine, slightly so in methyl or ethyl alcohol, and insoluble in light petroleum. M. A. W.

meso-Phenylated Derivatives of Anthracene. A Correction.

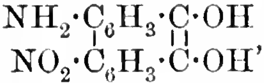
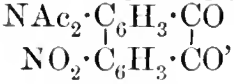
CARL LIEBERMANN and SIMON LINDENBAUM (*Ber.*, 1905, **38**, 3802—3804). —The compound previously formulated as

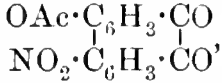


$$OH\cdot C(OPh)<\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}>CPh\cdot OH$$

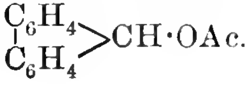
and its monoacetyl derivative (Abstr., 1905, i, 522) are shown to be

9-hydroxyphenyl-9-phenylanthrone,  $CO{<}\begin{array}{c}C_6H_4\\C_6H_4\end{array}{>}CPh\cdot C_6H_4\cdot OH$, and its acetyl derivative. T. M. L.

Phenanthrene Derivatives. XVII. Conversion of 4 : 5-Dinitrophenanthraquinone into 4 : 5-Aminohydroxyphenanthraquinone. Julius Schmidt and Fritz Leipprand (*Ber.*, 1905, **38**, 3733—3737. Compare Abstr., 1901, i, 76, 464; 1902, i, 29, 715, 757, 797; 1903, i, 557, 691; 1904, i, 69, 70, 71, 1033, 1034).—4 : 5-Dinitrophenanthraquinone (Abstr., 1904, i, 71) is readily reduced by stannous chloride at 30° in the presence of hydrochloric and acetic acids to the *hydrochloride* of *4-nitro-5-aminophenanthraquinol*,  $\begin{array}{l}NH_2\cdot C_6H_3\cdot C\cdot OH\\NO_2\cdot C_6H_3\cdot C\cdot OH\end{array}$, which forms yellowish-red crystals readily soluble in water. 4-*Nitro-5-aminophenanthraquinone* is formed as a dark brown powder when a current of air is passed through a paste of the hydrochloride and saturated sodium carbonate solution; it decomposes when slowly heated, and dissolves but sparingly in most organic solvents. The *diacetyl* derivative,  $\begin{array}{l}NAc_2\cdot C_6H_3\cdot CO\\NO_2\cdot C_6H_3\cdot CO\end{array}$, crystallises in dark brown needles and melts at 280°.

4-*Nitro-5-hydroxyphenanthraquinone* is obtained when the corresponding nitroamino-compound is diazotised and the clear solution of the diazonium salt heated on the water-bath. It is a reddish-brown powder, melts and decomposes at 240°, and dissolves readily in alcohol, ether, or ethyl acetate to deep red solutions. It also dissolves in concentrated sulphuric acid and in alkalis, and has such pronounced acidic properties that it can be completely removed from its ethereal solutions by shaking with sodium carbonate solution. The *acetyl* derivative,  $\begin{array}{l}OAc\cdot C_6H_3\cdot CO\\NO_2\cdot C_6H_3\cdot CO\end{array}$, crystallises in yellowish-green needles; when heated, it sinters at 200° and melts and decomposes at 220°.

4-*Amino-5-hydroxyphenanthraquinone* is obtained by reducing the nitroamino-compound to aminohydroxyphenanthraquinol hydrochloride, and then decomposing this with sodium carbonate in presence of atmospheric oxygen. It forms a black powder and dissolves sparingly in the usual organic solvents. J. J. S.

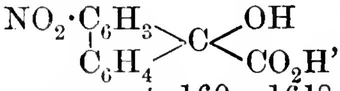
Phenanthrene Derivatives. XVIII. Conversion of Phenanthrene into Fluorene Compounds. Julius Schmidt and Karl Bauer (*Ber.*, 1905, **38**, 3737—3757. Compare Anschütz and Schultz, *Annalen*, 1879, **196**, 50; R. Meyer and Spengler, Abstr., 1905, i, 219).—The 2-nitro-, 4-nitro-, 2 : 7-dinitro-, 4 : 5-dinitro-, 2-bromo-, 2 : 7-dibromo-, and 2 : 7-bromonitro-derivatives of phenanthraquinone, when heated with aqueous 10 per cent. sodium or potassium hydroxides, are converted into the corresponding derivatives of 9-hydroxyfluorene-9-carboxylic acid, and when these are heated with acetic anhydride in the atmosphere of hydrogen they lose carbon dioxide and yield derivatives of fluorenyl acetate,  $\begin{array}{c}C_6H_4\\C_6H_4\end{array}{>}CH\cdot OAc$.

When boiled with acetic anhydride, with water, or with alkalis in the presence of air, they yield derivatives of fluorenone.

The nature of the substituents in the phenanthraquinone molecule affects the transformation; thus, with 10 per cent. potassium hydroxide, phenanthraquinone itself requires a temperature of 80°, and the mononitro-derivatives of from 50—65°, whilst the dinitro-derivatives are transformed at 15°. Bromine substituents also facilitate the transformation, but not to the same extent.

The stability of the hydroxyfluorenecarboxylic acids is diminished by the presence of nitro-groups.

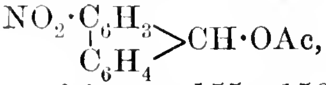
2-*Nitro-9-hydroxyfluorene-9-carboxylic acid*,



$\genfrac{}{}{0pt}{}{NO_2\cdot C_6H_3}{C_6H_4}>C<\genfrac{}{}{0pt}{}{OH}{CO_2H}$,

forms yellowish-brown prisms, melts and decomposes at 160—161°, and is decomposed when boiled with water. It dissolves readily in ether, chloroform, or benzene, and all solutions are coloured brown.

2-*Nitrofluorenyl acetate*,

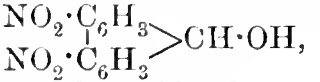


$\genfrac{}{}{0pt}{}{NO_2\cdot C_6H_3}{C_6H_4}>CH\cdot OAc$,

crystallises from acetic acid in yellow needles melting at 155—156°, and when boiled with concentrated hydrochloric acid yields a *compound* melting at 129—130°.

4-*Nitro-9-hydroxyfluorene-9-carboxylic acid* crystallises in colourless needles, melts at 156—158°, may be crystallised quickly from hot water, and is only sparingly soluble in benzene or chloroform. The solution in *N*/10 sodium hydroxide yields characteristic precipitates with silver nitrate, lead acetate, and cupric sulphate. 4-*Nitrofluorenyl acetate* crystallises from alcohol in colourless plates, melts at 112—113°, and is readily soluble in the usual organic solvents. When hydrolysed with concentrated hydrochloric acid, it yields a *compound*, $C_{13}H_9O_4N$, melting at 105—107°. 4-*Nitrofluorenone*, $C_{13}H_7O_3N$, is obtained together with the *compound* $C_{26}H_{14}O_3N_2$ when the carboxylic acid is boiled with water. It crystallises from acetic acid, in which it is moderately soluble, and melts at 173—174°. Its *oxime*, $C_{13}H_8O_3N_2$, crystallises in dark green needles which melt and decompose at 255—256°. The *semicarbazone* forms a brown powder, which is not molten at 350°.

2 : 7-*Dinitro-9-hydroxyfluorene-9-carboxylic acid* is formed together with 2 : 7-*dinitrophenanthraquinhydrone* when 2 : 7-dinitrophenanthraquinone (5 grams) is treated with 10 per cent. potassium hydroxide for fifteen minutes at the ordinary temperature, and then immediately acidified with ice-cold dilute sulphuric acid. The acid crystallises in colourless needles, turns brown at 130°, and melts and decomposes at about 280°. It has a bitter taste and dissolves readily in ethyl alcohol or acetone. 2 : 7-*Dinitrofluorenyl acetate* crystallises in colourless needles, melts at 244°, and decomposes at 247°; the corresponding *alcohol*,



$\genfrac{}{}{0pt}{}{NO_2\cdot C_6H_3}{NO_2\cdot C_6H_3}>CH\cdot OH$,

forms colourless needles, melts at 212°, and is readily oxidised to 2 : 7-dinitrofluorenone, which crystallises from glacial acetic acid in yellow needles melting at 290°. It is identical with Schultz' dinitrofluorenone (Abstr., 1880, 814). The *oxime* melts and decomposes at 285—286°, the phenylhydrazone crystallises in dark red, glistening prisms which melt and decompose at 263—264° (compare Abstr., 1896, i, 174), the *semicarbazone* crystallises in pale yellow needles and is not molten at 350°.

4:5-*Dinitro-9-hydroxyfluorene-9-carboxylic acid* forms brownish yellow needles, melts and decomposes at 140°, and is moderately soluble in ether, alcohol, or chloroform, and readily in acetone.

4:5-*Dinitrofluorenyl acetate* forms colourless needles melting at 220—221°; the corresponding *alcohol* melts at 201—202°, and 4:5-*dinitrofluorenone* crystallises in yellow needles; these change colour at 330°, but are still solid at 350°. The *oxime* melts at 267—268°, the *phenylhydrazone* melts and decomposes at 241°, and the *semicarbazone* at 288°.

2-*Bromo-9-hydroxyfluorene-9-carboxylic acid* forms colourless needles, melts and decomposes at 213°, and is only sparingly soluble in benzene. 2-*Bromofluorenyl acetate* melts at 70—72° and dissolves readily in the usual solvents. 2-*Bromofluorenyl alcohol* melts at 100—102°. 2-*Bromofluorenone*, $C_{13}H_7OBr$, crystallises from acetic acid in yellow needles and melts at 134°. The *oxime* melts at 194—195°, the *phenylhydrazone* crystallises in brick-red needles and melts at 148°, the *semicarbazone* melts at about 235°.

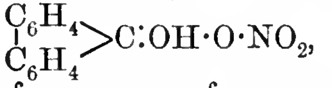
2:7-*Dibromo-9-hydroxyfluorene-9-carboxylic acid* forms white needles and melts and decomposes at 280°. 2:7-Dibromofluorenone is identical with Holm's dibromofluorenone (Abstr., 1883, 921; Werner, 1904, i, 863). The *oxime*, $C_{13}H_7ONBr_2$, crystallises in pale yellow needles and melts and decomposes at 235°, the phenylhydrazone forms orange-red needles and melts at 192—193° (compare Abstr., 1896, i, 174), and the *semicarbazone* begins to decompose at 240°, but is still solid at 350°.

2-*Bromo-7-nitro-9-hydroxyfluorene-9-carboxylic acid* forms a reddish-brown powder and begins to decompose at 160°. 2-*Bromo-7-nitrofluorenone* forms yellow needles and melts at 230°; it can also be obtained by nitrating 2-bromofluorenone. The *oxime*, $C_{13}H_7O_3N_2Br$, melts and decomposes at 249°, the *phenylhydrazone* forms red needles and melts and decomposes at 245°, the *semicarbazone* is still solid at 350°.

When 9-hydroxyfluorene-9-carboxylic acid is heated for an hour with acetic anhydride on the water-bath, it yields an *isomeride* melting at 212°, and less readily soluble in the ordinary solvents. J. J. S.

Action of Nitric Acid on Fluorenone, and Derivatives of the Nitro-compounds thus obtained.

Julius Schmidt and Karl Bauer (*Ber.*, 1905, **38**, 3758—3763).—*Fluorenone nitrate*,

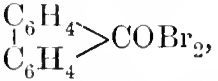


$$\left.\begin{array}{l}C_6H_4\\ |\\ C_6H_4\end{array}\right>C{:}OH\cdot O\cdot NO_2,$$

is formed by the action of an excess of concentrated nitric acid of sp. gr. 1·45 on fluorenone at 0°. It is unstable and on exposure to the atmosphere liberates nitric acid. 2:7-Dinitrofluorenone (Schultz, Abstr., 1880, 814) is obtained by boiling the ketone with fuming nitric acid of sp. gr. 1·52.

2:6:7-*Trinitrofluorenone* is obtained when the ketone is boiled for two hours with a mixture of fuming nitric acid and concentrated sulphuric acid. It crystallises from glacial acetic acid in pale yellow, glistening needles, melts at 180—181°, and dissolves readily in most organic solvents. Its constitution follows from the fact that when oxidised it yields 3 : 4-dinitrobenzoic acid and that it may be prepared by further nitration of the 2 : 7-dinitro-derivative. The *oxime*, $C_{13}H_6O_7N_4$, crystallises from alcohol in practically colourless needles and melts and decomposes at 260°. The *phenylhydrazone* forms glistening, violet plates and melts and decomposes at 276°. The *semicarbazone* melts and decomposes at 299°. When reduced with tin and hydrochloric acid, the trinitro-derivative yields 2 : 6 : 7-*triaminofluorenyl alcohol*, which is extremely unstable. The *hydrochloride*, $C_{13}H_{16}ON_3Cl_2$, is readily soluble in water but insoluble in alcohol. The *picrate* begins to decompose at 175°. 2 : 6 : 7-*Triaminofluorenone*, $C_{13}H_{11}ON_3$, melts and decomposes at 198° and is extremely unstable. The *hydrochloride* forms black plates. J. J. S.

Action of Bromine on Fluorene and on Fluorenone. JULIUS SCHMIDT and KARL BAUER (*Ber.*, 1905, **38**, 3764—3768. Compare Fittig and Schmitz, Abstr., 1879, i, 174).—Fittig and Schmitz' β-dibromofluorene is the 2 : 7-derivative, as it yields on oxidation 2 : 7-dibromofluorenone (this vol., i, 27). When fluorene is brominated in direct sunlight in chloroform solution, the chief product is 2 : 6(?) : 7-*tribromofluorene*, which crystallises from alcohol in stout needles melting at 200°. When oxidised, it yields a tribromofluorenone identical with the product obtained by brominating 2 : 7-dibromofluorenone. Fluorenone unites with bromine in much the same manner as phenanthraquinone (Abstr., 1904, i, 1033), yielding the *dibromide*,

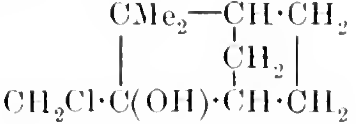


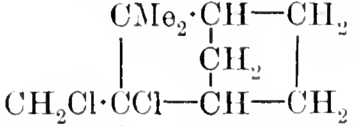
$$\left.\begin{array}{l}C_6H_4\\ |\\ C_6H_4\end{array}\right>COBr_2,$$

which, however, has not been obtained in a pure state. When heated with bromine water, fluorenone at 100° yields 2-bromofluorenone, or, at 150°, 2 : 7-dibromofluorenone (*loc. cit.*). 2 : 6(?) : 7-*Tribromofluorenone*, obtained by heating the 2 : 7-dibromo-derivative with bromine and water at 160—170°, crystallises from glacial acetic acid in yellow needles melting at 180—181°. The *oxime*, $C_{13}H_6ONBr_3$, melts and decomposes at 243°, the *phenylhydrazone* at 227°, and the *semicarbazone* forms pale yellow needles which are still solid at 350°. J. J. S.

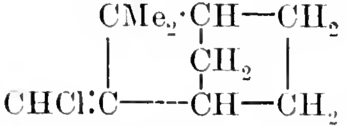
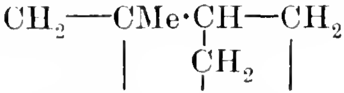
Preparation of Camphor from *iso*Borneol. CHEMISCHE FABRIK AUF AKTIEN VORM. E. SCHERING (D.R.-P. 161523. Compare Abstr., 1905, i, 709).—Oxygen or atmospheric air may be used to oxidise *iso*borneol to camphor. Thus, when *iso*borneol is heated at 160° and volatilised in a current of oxygen, the vapour being led over copper gauze spirals at 180°, the product contains about 20 per cent. of camphor. Air may be employed instead of oxygen, the temperature of the liquid then being 175°. C. H. D.

Action of Hypochlorous Acid on Camphene. KAZIMIR SLAWIŃSKI (*Bull. Acad. Sci. Cracow*, 1905, 491—500).—The action of hypochlorous acid on camphene leads to the formation of camphene dichloride and camphene chlorohydrin, which are solid, and a mixture of three liquid chlorocamphenes, $C_{10}H_{15}Cl$.

Camphene chlorohydrin,  , is isolated from its mixture with the dichloride, than which it is more soluble in methyl alcohol, in the form of its *acetate*, which is obtained also by the action of silver acetate on the dichloride. It melts at 52·5°, and on hydrolysis yields the *anhydride*, $C_{10}H_{16}O$, which is formed also when the mixture of dichloride and chlorohydrin is boiled with aqueous potassium hydroxide; the *dichloride*,

 ,

which melts at 139—140°, remaining unchanged. The anhydride boils at 99—100·5° under 20 mm. pressure, has the sp. gr. 0·9372 at 0°/0° or 0·9254 at 15°/0°, and forms a crystalline *additive* compound with sodium hydrogen sulphite, which, on hydrolysis, yields iso*camphenilanaldehyde*, $C_{10}H_{16}O$. This boils, in an atmosphere of hydrogen, at 82—84° under 12 mm. pressure, has the sp. gr. 0·9571 at 0°/0°, or 0·9284 at 15°/0°, and, when distilled in air, is oxidised to *iso*camphenilanic acid melting at 118°. The aldehyde is probably a stereoisomeride of camphenilanaldehyde (Bredt and Jagelki, Abstr., 1900, i, 134).

The mixture of liquid chloro-compounds contains *chlorocamphene*,  , *chlorocyclene*,  , and a *chloro*-compound, $C_{10}H_{15}Cl$, which is not a derivative of camphene. On reduction with sodium and alcohol, the mixture of chloro-compounds yields camphene and cyclene, a portion remaining unreduced. When oxidised with potassium permanganate, the mixture yields camphenilone, melting at 38°, traces of a neutral *product*, melting at 205°, dehydrocamphenilic acid, melting at 150·5°, camphenilic acid, melting at 172°, and a small quantity of a liquid acid. The chloro-compound, remaining unoxidised, has the sp. gr. 1·0498 at 0°/0° or 1·347 [? 1·0347] at 17°/0°, and does not react with alcoholic silver nitrate.

The action of sodium acetate on the mixture of chloro-compounds, at 140°, leads to the elimination of the one-third of the mixture which interacts with silver nitrate, by formation of an *acetate*, which boils at 106—110° under 13 mm. pressure, and on hydrolysis yields a mixture of *alcohols*, $C_{10}H_{16}O$, melting at 45—50°; on oxidation with potassium permanganate, this forms two neutral substances, melting at 205—207° and 150°, respectively, traces of dehydrocamphenilic acid, and a liquid acid. The chloro-compounds remaining after treatment of the mixture with sodium acetate are converted into the acetate of camphene chlorohydrin by the action of acetic and sulphuric acids.

The camphene obtained from *iso*borneol consists of a mixture of true camphene, cyclene, and the hydrocarbon, which corresponds with camphenocamphoric acid. G. Y.

Caoutchouc. Relations existing between the Hydrocarbons from Caoutchouc and Gutta-percha. Carl D. Harries (*Ber.*, 1905, **38**, 3985—3989).—The hydrocarbon, $C_{10}H_{16}$, of gutta-percha (compare Tschirch and Müller, Abstr., 1905, i, 452), when subjected to the action of ozone in chloroform solution (compare Harries, Abstr., 1904, i, 757; 1905, i, 364), gives an ozonide, $C_{10}H_{16}O_6$, which resembles the ozonide derived from caoutchouc in giving a mixture of lævulinaldehyde and lævulic acid when decomposed by steam; the proportions of these two substances are, however, reversed. The opinion is expressed that the fundamental hydrocarbons, $C_{10}H_{16}$, of caoutchouc and gutta-percha are actually identical, both being probably 1 : 5-dimethyl*cyclo*octo-$\Delta^{1:5}$-diene, and that the ozonides are stereoisomeric derivatives of this hydrocarbon. Provisional formulæ are suggested. W. A. D.

New Fossil Copal (Java Copal). Karl Dieterich (*Chem. Centr.*, 1905, ii, 1430—1431; from *Pharm. Post.*, **38**, 551—553).—A sample of a Java fossil copal consisted of pieces about the size of a walnut which had a turbid or milky appearance, and when ground formed a brownish-grey powder. The copal contained fragments of pyrites and carbon, and had a lustrous, conchoidal fracture; it was as hard as rock salt and had a sp. gr. 1·033—1·041. When heated, it sintered at 160—170°, began to melt at 175°, and formed a clear liquid at 178°. The copal lost 0·265 per cent. at 100°, and yielded 2·44 per cent. of ash, which consisted mainly of ferric oxide; it had an acid number 4·55—5·07, saponification number 14·54—18·03, ester number 9·98—12·96, and Hübl-Waller iodine number 50·86—54·66, but did not contain nitrogen, volatile acids, ethereal oils, or bitter principles. 82·58 per cent. of the copal was insoluble in 96 per cent. alcohol, 41·63 in ether, 80·61 in acetone, 2·59 in chloroform, 3·92 in benzene, 5·84 in carbon disulphide, 92·97 in wood spirit, 2·24 in light petroleum, 95·29 in a 60 per cent., and 90·76 in an 80 per cent. solution of chloral hydrate, 73·36 in dichlorohydrin, 53·96 in epichlorohydrin, and 2·58 in oil of turpentine. When submitted to dry distillation, it did not form a sublimate, and when heated to 120° it yielded 1·07 per cent. of a thin, bright yellow oil together with white vapours, which escaped condensation. The oil contained water and had an odour similar to that of turpentine; it had n_D 1·4803 at 17·5° and 1·4812 at 17°. On raising the temperature to 280°, 15·67 per cent. of a brownish-yellow, highly refractive oil was obtained which had an empyreumatic odour, a sp. gr. 0·921 at 15°, n_D 1·5116 at 17°, and iodine number 87·24—96·53. The third fraction, which distilled at 280—300°, consisted of 22·61 per cent. of a dark oil, which had an empyreumatic odour, remarkably similar to that of oil of wormwood; it had a sp. gr. 0·928 at 15°, and iodine number 113·48—120·74. The presence of tanacetone could not be detected. When the temperature was further raised to 360°, 19·03 per cent. of a dark reddish-brown oil distilled, which had a penetrating empyreumatic odour; it had a sp. gr. 0·920 at 15° and iodine number 98·10—102·68. The last fraction, obtained at temperatures above 360°, was equal to 12·93 per cent. of the total weight of the copal, and formed a greenish-brown, viscous oil, which had an odour similar to that of turpentine; it had a sp. gr. 0·9805 at 15°, and iodine number 42·68. The residue, which amounted to 13·87 per cent., consisted of tar and carbon. The Java fossil copal does not appear to be related to any of the known kinds of copal. E. W. W.

Japan Lacquer (Ki-Urushi). Alexander Tschirch and A. B. Stevens (*Arch. Pharm.*, 1905, **243**, 504—553).—The paper contains an account of work done previously on the subject, a description of the specific action of the poison (producing local dermatitis) contained in the lacquer, this poison being shown not to be volatile, as hitherto supposed, but to consist of an oily substance soluble in light petroleum, and a summary of numerous oxydases, in which connection it is shown that enzymes of this character are associated with many "gums" ("*Gummis*"), and the name of *gummases* is proposed for such enzymes.

Owing to the difficulties attending the investigation, the results were somewhat meagre. Of the sample examined, 72 per cent. dissolved in alcohol; water then dissolved 4·0 per cent., leaving 2·3 per cent. of residue; the remaining 21 per cent. must have been water. The portion soluble in alcohol, called by Yoshida (Trans., 1883, **43**, 472) urushic acid or lacquer acid, and by Bertrand laccol, has not the character of an acid, and in consequence the name of *urushin* is proposed for it. Under the influence of various reagents, including acids, alkali hydroxides, and the enzyme contained in the lacquer when moist air is present, urushin is transformed into an exceedingly stable substance, *oxyurushin* (Yoshida's oxyurushic acid), to which fact the value of the lacquer is due. It is noteworthy that both urushin and oxyurushin contain nitrogen, for they are the first substances belonging to the class of resins in which nitrogen has been detected. Urushin contains C 71·0—73·6, H 7·8—10·5, N 0·2—1·8, ash 0·2—1·2; oxyrushin: C 70·9—71·8, H 8·1—8·3, N 0·1—1·6, ash 0·0—0·8 per cent.

Urushin can be separated into two fractions respectively soluble (78 per cent.) and insoluble in light petroleum. The soluble fraction can be separated further into a non-volatile *poison* and a mixture of *gum* and *enzyme* (lacquer-gummase, Bertrand's laccase, Abstr., 1895, i, 385, 386) which could not be separated into its constituents. This mixture contained C 41·7, H 6·0, N 0·61, ash 5·2 per cent.; it yields pyrrole, not ammonia, when heated with solid potassium hydroxide; mucic acid, calcium oxalate, and tartaric acid when oxidised with nitric acid; and *r* and *r*+*l*-sorbinazone when hydrolysed with dilute sulphuric acid and treated with phenylhydrazine. The lacquer also contains acetic acid. C. F. B.

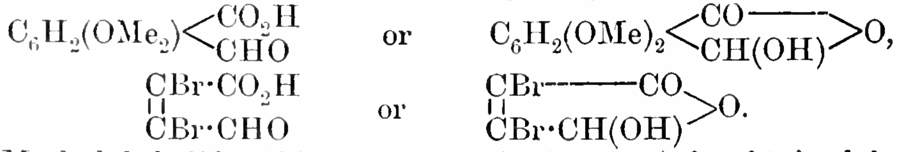
Prulaurasin, a Crystalline Cyanogenetic Glucoside obtained from the Leaves of Cherry Laurel. Henri Hérissey (*Compt. rend.*, 1905, **141**, 959—961).—Previous attempts to extract the cyanogenetic principle from the leaves of the cherry-laurel in a pure state have not been successful (compare Lehmann, *Neues Rep. Pharm.*, 1874, **23**, 449; Jouck, Abstr., 1905, i, 912), and in the present paper details are given of a method whereby the crystalline glucoside prulaurasin can be obtained from the fresh leaves of the plant. *Prulaurasin*, $C_{14}H_{17}O_6N$, crystallises from a mixture of ethyl acetate and toluene or chloroform in long, slender, colourless, flexible needles melting at 120—122°, has $\alpha_D - 52·75°$, and a slightly bitter taste. is readily soluble in water, alcohol, or ethyl acetate, slightly soluble in ether. It is hydrolysed by emulsin, yielding hydrogen cyanide, dextrose, and benzaldehyde, and is therefore an isomeride of Fischer's benzalnitrile-glucoside (Abstr., 1895, i, 553) and of Bourquelot and Danjou's sambunigrin (Abstr., 1905, i, 912).

M. A. W.

The Saponin of the White Soapwort. LEOPOLD ROSENTHALER (*Arch. Pharm.*, 1905, **243**, 496—504).—Gypsophila-saponin, obtained from the root of the Levantine soapwort, appears to be a mixture of two homologues, $C_{18}H_{28}O_{10}$ and $C_{19}H_{30}O_{10}$. When it is hydrolysed, sapogenin, an arabinose, and another sugar are formed in about equal quantities.

C. F. B.

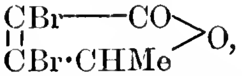
Action of Grignard's Reagent on *o*- or γ-Aldehydo-acids. HUGO SIMONIS, E. MARBEN, and E. MERMOD (*Ber.*, 1905, **38**, 3981—3985. Compare Liebermann, Abstr., 1886, 550; Bistrzycki, *ibid.*, 1888, 1210; 1890, 969; 1891, 746).—The reaction between *o*- and γ-aldehydo-acids and Grignard's reagent has been studied in order to settle the question as to whether the compounds have the aldehydo-constitution or the isomeric hydroxylactone formula:



$$C_6H_2(OMe_2){<}\begin{smallmatrix}CO_2H\\CHO\end{smallmatrix} \quad \text{or} \quad C_6H_2(OMe)_2{<}\begin{smallmatrix}CO\text{———}\\CH(OH)\end{smallmatrix}{>}O,$$

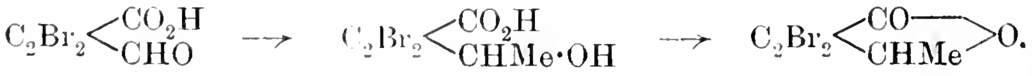
$$\begin{matrix}CBr{\cdot}CO_2H\\ \Vert\\ CBr{\cdot}CHO\end{matrix} \quad \text{or} \quad \begin{matrix}CBr\text{———}CO\\ \Vert\\ CBr{\cdot}CH(OH)\end{matrix}{>}O.$$

α-Methylphthalide (Giebe, Abstr., 1897, i, 62) is obtained by the action of an excess of methyl magnesium iodide on phthalaldehydic acid and α-methylmeconine (m. p. 101°) by the action of the same reagent on opianic acid.

3 : 4-*Dibromo-2-methyldihydrofuranone*,  $\begin{matrix}CBr\text{——}CO\\ \Vert\\ CBr{\cdot}CHMe\end{matrix}{>}O$, obtained from magnesium methyl iodide and mucobromic acid, crystallises from water in flat needles melting at 69·5°. The corresponding *ethyl* derivative crystallises from light petroleum and melts at 51·5°.

3 : 4-*Dichloro-2-methyldihydrofuranone* distils at 120° under 12 mm. pressure and the corresponding *ethyl* compound at 109—110° under 11 mm. pressure.

These reactions indicate the aldehydic structure of all the acids Thus:



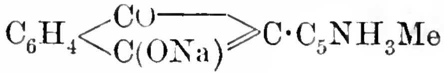
$$C_2Br_2{<}\begin{smallmatrix}CO_2H\\CHO\end{smallmatrix} \longrightarrow C_2Br_2{<}\begin{smallmatrix}CO_2H\\CHMe{\cdot}OH\end{smallmatrix} \longrightarrow C_2Br_2{<}\begin{smallmatrix}CO\text{——}\\CHMe\end{smallmatrix}{>}O.$$

J. J. S.

Arylamine Derivatives of Furfuraldehyde and their Conversion into Pyridine Compounds. Theodor Zincke and G. Muhlhausen (*Ber.*, 1905, **38**, 3824—3829).—The dianilide, $C_{17}H_{16}ON_2$, probably $C_4OH_3\cdot CH(C_6H_4\cdot NH_2)_2,H_2O$, prepared by the action of aniline and its hydrochloride on furfuraldehyde (Stenhouse, *Annalen*, 1870, **156**, 199), yields a *hydrobromide* which crystallises from hot alcohol in long, violet-red needles and melts and decomposes at 165—166°. The *di*-p-*toluidide* yields a *hydrochloride*, $C_{19}H_{20}ON_2,HCl$, which crystallises from alcohol in long, slender, violet-red needles and melts and decomposes at 173—178°

3-*Hydroxy*-1-*phenylpyridinium chloride*, $OH\cdot C_5NH_4PhCl$, prepared by boiling the hydrobromide of the dianilide with alcohol or acetic acid, crystallises from absolute alcohol in stout, colourless needles or spangles, or in compact, rhombic crystals, and melts at 210—212°; the *platinichloride* crystallises from hot water in long, orange-yellow needles and melts and decomposes at 204—206° after losing its water of crystallisation at 100°; the *bromide*, $C_{11}H_{10}ONBr$, forms colourless needles and melts at 175°.

3-*Hydroxy*-1-p-*tolylpyridinium chloride*, $OH\cdot C_5NH_4Cl\cdot C_6H_4Me$, crystallises from hot water in long, broad spangles or in small needles, melts at 210—212°, and is more soluble than the phenyl compound; the *platinichloride* crystallises from hot water in orange-yellow, hydrated needles and melts and decomposes at 216°. T. M. L.

2-Methyl-6-pyrophthalone. A. Scholze (*Ber.*, 1905, **38**, 4022). —The formula of the sodium salt of 2-methyl-6-pyrophthalone should be  $C_6H_4<\begin{matrix}CO\text{——}\\C(ONa)\end{matrix}>C\cdot C_5NH_3Me$ instead of that given formerly (Abstr., 1905, i, 825). W. A. D.

Influence of Light and Heat on the Chlorination and Bromination of Homologues of Thiophen. II. St. Opolski (*Bull. Acad. Sci. Cracow*, 1905, 548—557. Compare Abstr., 1905, i, 367).—The substitution of halogen in the ring of 2-alkylthiophens takes place in position 5. The bromination product of 2-methylthiophen is 5-bromo 2-methylthiophen, as when treated with methyl iodide and sodium at the laboratory temperature it is converted slowly into 2 : 5-dimethylthiophen. Bromination of 2-ethylthiophen at high temperatures leads to the formation of 5 bromo-2-ethylthiophen, which is formed also under the influence of light (*loc. cit.*).

Chlorination of 2-ethylthiophen at its boiling point or under the influence of light leads to the formation of 5-*chloro*-2-*ethylthiophen*, which is a liquid of mild odour, boils at 85—88° under 37 mm. or at 175·5° (corr.) under 737 mm. pressure, does not solidify at $-75°$, and becomes yellow on exposure to light. It has the sp. gr. 1·1629 at 12·3°/4° and n_D 1·5330 at 12·3°, and gives the indophenin and Laubenheimer's colour reactions only indistinctly and with difficulty.

On chlorination under the influence of heat or light, 2-butylthiophen yields chiefly 5-*chloro*-2-*butylthiophen*, which is a colourless liquid of mild odour, becomes yellow on exposure to light, boils at 117—118° (corr.) under 38 mm. pressure, and has the sp. gr. 1·0812 at 17°/4° and n_D 1·5162. *5-Bromo-2-butylthiophen*, formed by bromination of 2-butylthiophen in the same manner, is a colourless liquid of mild odour, boils at 138·5° (corr.) under 42 mm. pressure, and has the sp. gr. 1·3369 at 20·5°/4°, and n_D 1·5398. 5-Chloro- and 5-bromo-2-butylthiophen give the colour reactions with isatin and phenanthraquinone only indistinctly and with difficulty.

3-Methylthiophen has the sp. gr. 1·0247 at 15·8°/4° and n_D 1·5218. When boiled with alcoholic ammonia, the product obtained on chlorination at the boiling point or under the influence of light yields only a small amount of a *substance* which forms a solid *hydrochloride* and a yellow, amorphous *platinichloride*. The chief product of the chlorination is *chloro-3-methylthiophen*, which is obtained as a colourless liquid boiling at 154° (corr.) under 733 mm. pressure; it has the sp. gr. 1·2197 at 19·6°/4°, and n_D 1·5394, and gives a green coloration with isatin in sulphuric acid solution and a glistening emerald-green coloration with phenanthraquinone and sulphuric acid in glacial acetic acid solution.

Bromination of 3-methylthiophen under the same conditions leads to the formation of bromo-3-methylthiophen, together with a considerable amount of a *product* substituted in the side-chain. This, when boiled with alcoholic ammonia, yields *trithienylamine*, $N(CH_2{\cdot}C_4H_3S)_3$?, which forms a white, crystalline *hydrobromide* and *hydrochloride* melting at 124·5—127°; these give yellow to red, amorphous *platinichlorides*. *Bromo-3-methylthiophen* is a colourless liquid, which becomes yellow on exposure to light, boils at 175° (corr.) under 729 mm., and has the sp. gr. 1·5844 at 17·5°/4°, and n_D 1·5731. It gives Laubenheimer's green coloration and a green coloration changing to blue with isatin.

The distillation residues obtained in the preparation of homologues of thiophen by Fittig's reaction are explosive, evolve hydrogen and acetylene when treated with water, and contain therefore probably sodium carbide together with unchanged sodium. G. Y.

Angostura Bases. HEINRICH BECKURTS and GUSTAV FRERICHS [and, in part, A. LACHWITZ] (*Arch. Pharm.*, 1905, **243**, 470—493. Compare Körner and Boehringer, Abstr., 1884, 341; Beckurts and others, Abstr., 1892, 642; 1896, i, 66; 1904, i, 84).—The *nitrate* with 1½H_2O, *dichromate*, and *acetate* of the monoacid base cusparine, $C_{20}H_{19}O_3N$, are described for the first time; the last loses its acetic acid when kept in a desiccator over sulphuric acid.

When a solution of cusparine in dilute hydrochloric acid is mixed with a limited amount of bromine dissolved in water and ammonia is added until the reaction is alkaline, crystalline *monobromocusparine*, $C_{20}H_{18}O_3NBr$, melting at 91°, is precipitated; the crystalline *hydrochloride*, *platinichloride*, and *aurichloride* were prepared and analysed; the last two melt at 210—212° and 188—190° respectively. When excess of bromine is added to a solution of cusparine in dilute hydrobromic acid, amorphous, yellow *bromocusparine tetrabromide*, melting at 163—164°, is precipitated; when this is treated with alcohol, it yields the yellow, amorphous *tribromide* melting at 163—165°; when heated at 105°, the *dibromide*, which melts at 163—166°; from a warm solution of any of these in alcohol, *bromocusparine hydrobromide*, melting at 239—241°, crystallises. Boiling with dilute potassium hydroxide solution, or reduction with either zinc and sulphuric acid or hydrogen sulphide, converts the tetrabromide into monobromocusparine itself.

With cusparine in chloroform solution, bromine yields a precipitate of monobromocusparine dibromide, whilst bromocusparine hydrobromide remains in solution. In acetic acid solution, bromine converts cusparine into monobromocusparine tribromide, together with some tetrabromide and bromocusparine hydrobromide.

When a solution of sodium hypochlorite is added to a solution of cusparine in acetic acid, yellow, amorphous *dichlorocusparine*, $C_{20}H_{17}O_3NCl_2,2H_2O$, is precipitated.

When excess of iodine solution is added to a solution of cusparine hydrochloride, the dark-coloured *hydriodide* of *cusparine di-iodide*, $C_{20}H_{19}O_3N,HI,I_2,2H_2O$, is precipitated; this crystallises unchanged from alcohol.

Ethylcusparine, $C_{22}H_{23}O_3N$, crystallises with 1 molecule of alcohol: the compound melts at 116°. The *hydrochloride* and *platinichloride* of this mono-acid base were analysed; the latter melts and decomposes at 186°.

Cusparine does not react with benzoyl chloride.

Of galipidine, $C_{19}H_{19}O_3N$, a monoacid base, the *hydriodide*, *sulphate*, and *hydrogen sulphate* were analysed. The base itself yields protocatechuic acid when heated with fused potassium hydroxide. From a solution of galipidine hydrobromide, excess of bromine precipitates the *pentabromide*, $C_{19}H_{19}O_3N,HBr,Br_5$; when heated at 105°, this leaves the dibromide, $C_{19}H_{19}O_3N,HBr,Br_2$, whilst when washed with cold alcohol, $C_{19}H_{19}O_3N,HBr,Br$ is obtained.

Galipidine methochloride, $C_{19}H_{19}O_3N,MeCl$, which crystallises in greenish-yellow needles, and the corresponding *platinichloride* and *aurichloride*, which melt at 187° and 119° respectively, were analysed. When the methiodide is warmed with dilute aqueous potassium hydroxide, the monoacid base, *methylgalipidine*, $C_{20}H_{21}O_3N$, is formed; this crystallises in needles and melts at 166°; its yellow *hydrochloride* and *platinichloride*, the latter melting and decomposing at 200°, were analysed.

When galipidine is heated with ethyl iodide for twelve hours at 100°, the *ethiodide*, $C_{19}H_{19}O_3N,EtI$, is formed; this crystallises with $1H_2O$ and melts at 102° to a milky liquid which becomes clear at 140—142°; the corresponding *aurichloride*, which is amorphous and melts at about 142°, was analysed.

Galipidine does not form additive compounds with methylene iodide, or with ethylene iodide or bromide. C. F. B.

Crystalline Alkaloid of Calycanthus Glaucus. II. Harry M. Gordin (*J. Amer. Chem. Soc.*, 1905, **27**, 1418—1429. Compare Abstr., 1905, i, 295).—A detailed description is given of calycanthine *nitrate*, sulphates, aurichloride, picrate, *oxalates*, *mercurichloride*, and *tartrates*. Calycanthine *nitrosoamine*, $C_{11}H_{13}N_2{\cdot}NO$, becomes brown at 172° and melts and decomposes at 175—176°. The alkaloid contains one methyl group attached to nitrogen. Attempts to prepare acetyl and benzoyl derivatives were unsuccessful. Methyl iodide converts calycanthine into a mixture of several substances which are at present under investigation. By the action of sulphuric acid on the alkaloid, a *sulphonic acid* is produced; its *barium* salt was prepared.

E. G.

[The Alkaloids of] Bocconia Cordata. JULIUS O. SCHLOTTERBECK and WALTER H. BLOME (*Pharm. Rev.*, 1905, **23**, 310—321. Compare Murrill and Schlotterbeck, Abstr., 1900, i, 686).—When β-homochelidonine is heated in a sealed tube with strong hydrochloric acid, methyl chloride is produced together with a mixture of substances which were not isolated. An attempt was made to effect the oxidation of the alkaloid with alcoholic solution of iodine, but without success. Phosphorus pentachloride reacts with β-homochelidonine with formation of a yellow, crystalline *substance* which melts and decomposes at about 198° and is apparently the hydrochloride of an alkaloid not containing substituted chlorine in its molecule. An acetyl derivative of β-homochelidonine could not be obtained. On fusing the alkaloid with potassium hydroxide, protocatechuic acid is produced.

E. G.

Formation of Incompletely Hydrogenated Pyridines by the Wyschnegradsky-Ladenburg Reaction. ALEXEI E. TSCHITSCHIBABIN (*Ber.*, 1905, **38**, 3834).—A question of priority (compare Königs and Bernhart, Abstr., 1905, i, 824; Tschitschibabin, Abstr., 1902, i, 825).

A Tetrahydroaldehydecollidine. [2-Methyl-5-ethyltetrahydropyridine.] WILHELM KÖNIGS and KARL BERNHART (*Ber.*, 1905, **38**, 3928—3933. Compare Abstr., 1905, i, 824; Dürkopf, Abstr., 1888, 817; Levy and Wolffenstein, Abstr., 1895, i, 683; 1896, i, 624; Marcuse and Wolffenstein, Abstr., 1901, i, 608).—Reduction of 2-methyl-5-ethylpyridine with sodium and boiling absolute alcohol leads to the formation of the tetrahydro- and hexahydro-bases; these are separated by conversion into the hydrobromides and treatment with cold acetone, in which 2-methyl-5-ethylpiperidine hydrobromide is insoluble. This crystallises from hot acetone in colourless needles and melts at 175°. 2-Methyl-5-ethyltetrahydropyridine hydrobromide, which is soluble in cold acetone, is converted into *2-methyl-5-ethyltetrahydropyridine dibromide hydrobromide*, $C_8H_{15}NBr_2,HBr$, by means of bromine in chloroform solution, which, after removal of copellidine and *iso*copellidine hydrobromides by extraction with cold ethyl acetate, crystallises from a mixture of chloroform and ethyl acetate in colourless needles and melts and decomposes at 187°.

2-Methyl-5-ethyltetrahydropyridine dibromide, $C_8H_{15}NBr_2$, is obtained on treatment of its hydrobromide with aqueous sodium carbonate, as an oil which has an odour faintly resembling that of camphor, volatilises on exposure to the air, is moderately stable towards permanganate in cold dilute sulphuric or nitric acid solution, and with sodium nitrite in sulphuric acid solution forms the *nitroso*-derivative. This separates from light petroleum in colourless crystals, melts at 106—107°, gives a green coloration with Liebermann's nitrosoamine reaction, and when boiled with concentrated hydrobromic acid loses the nitroso-group and forms the hydrobromide.

2-*Methyl-5-ethyltetrahydropyridine*, $C_8H_{15}N$, is obtained in the form of its *hydrobromide*, $C_8H_{15}N,HBr$, by reducing the dibromide hydrobromide with zinc dust and dilute sulphuric acid at the laboratory temperature and treating the product with hydrobromic acid. The hydrobromide forms a colourless, crystalline mass, melts at 86—93°, or, after heating at 100°, at 98—99°, and with bromine in chloroform solution forms the dibromide hydrobromide. The base is a mobile, colourless oil, which has a pyridine-like odour and distils at 167—168° under 720 mm. pressure. The *oxalate* forms a colourless, crystalline powder and melts at 153—155°; the *ditartrate* is easily soluble in water or alcohol; the *picrate* forms yellow plates melting at 138—141°; the crystalline *aurichloride* melts at 83°; the yellow, crystalline *platinichloride* melts and decomposes at 190°. In dilute sulphuric acid solution, the base decolorises potassium permanganate at 0°; with carbon disulphide in ethereal solution, it forms the crystalline *thiocarbamate*, which melts at 73—74°. The base interacts with phenylthiocarbimide with development of heat and formation of an *oil* which solidifies to a crystalline mass melting at 80°. G. Y.

Compounds of Quinquevalent Chromium. RUDOLF F. WEINLAND and WALTER FRIDRICH (*Ber.*, 1905, **38**, 3784—3787).—*Pyridinium tetrachlorohydroxychromanate*, $C_5NH_5,CrCl_4{\cdot}OH,H_2O$, formed by the successive action of concentrated hydrochloric acid and pyridine on chromic acid at 10—12°, crystallises in glistening, reddish-brown leaflets or microscopic, orange-yellow, hexagonal plates.

Quinolinium tetrachlorohydroxychromanate, $C_9NH_7,CrCl_4{\cdot}OH,2H_2O$, prepared in similar manner, crystallises in glistening, reddish-brown needles or microscopic, long, orange-yellow plates, and decomposes on exposure to air, becoming orange-red with loss of chlorine.

G. Y.

Condensation of 2:4:6-Trimethylpyridine with Benzaldehyde. WILHELM KÖNIGS and ALFONS VON BENTHEIM (*Ber.*, 1905, **38**, 3907—3911. Compare Königs and Mengel, Abstr., 1904, i, 527).—When heated with 1 mol. of benzaldehyde and zinc chloride in a sealed tube at 170—180°, 2:4:6-trimethylpyridine yields the monobenzylidene derivative (2:4-dimethyl-α-stilbazole, Dubke, Abstr., 1894, i, 207) without intermixture of the alkine; the *platinichloride* melts at 245° (m. p. 230—232°, Dubke). Oxidation of the dimethylstilbazole with nitric acid leads to the formation of 2:4-dimethylpyridine-6-carboxylic acid (Altar, Abstr., 1887, 378).

When heated with 3 mols. of benzaldehyde and zinc chloride in a sealed tube at 170—180°, 2:4:6-trimethylpyridine forms the *tribenzylidene* derivative [2:4:6-*tristyrylpyridine*], $C_5NH_2(CH{:}CHPh)_3$, which crystallises in glistening, colourless needles, melts at 187—188°, dissolves readily in benzene, chloroform, or carbon disulphide, forming blue, fluorescent solutions which become yellow on addition of a trace of acid. The *acetate* crystallises from glacial acetic acid as a yellow salt with blue fluorescence which easily loses acetic acid; the *picrate*,

$C_{29}H_{23}N,C_6H_3O_7N_3,\frac{1}{2}C_3H_6O$, crystallises in golden needles and melts at 235—236°; the *platinichloride* forms a yellow powder. When oxidised with nitric acid, tristyrylpyridine yields pyridine-2 : 4 : 6-tricarboxylic acid (Voigt, Abstr., 1885, 812). G. Y.

Condensations of 2-Methyl-5-ethylpyridine and of 2:4-Lutidine with Aldehydes. G. Langer (*Ber.*, 1905, **38**, 3704—3709. Compare Abstr., 1888, 65, 608; 1890, 1437).—*4′-Methyl-5-ethyl-2-stilbazole*, $C_5NH_4Et\cdot CH:CH\cdot C_6H_3Me$, obtained by heating 2-methyl-5-ethylpyridine and *p*-tolualdehyde with zinc chloride at 210° for sixteen hours, crystallises from alcohol in colourless needles melting at 94°, and readily soluble in alcohol, ether, chloroform, or glacial acetic acid. The *hydrochloride*, $C_{16}H_{17}N,HCl$, is precipitated from its alcoholic solution by ether as small, yellow needles. The *mercurichloride* melts at 227°, the *picrate* at 201—202°, the *methiodide* at 212°, and the *ethiodide* at 233°. The corresponding *stilbazoline*, $C_{16}H_{25}N$, distils at 202—203° under 14 mm. pressure. Its salts form pasty masses. *4′-Methyl-5-ethyldihydro-2-stilbazole*, $C_{16}H_{19}N$, obtained by reducing the stilbazole with hydriodic acid at 160°, distils at 198° under 18 mm. pressure. The *hydrochloride* crystallises in yellow needles and melts at 42°; the *platinichloride* forms reddish-yellow needles and melts at 156—157°.

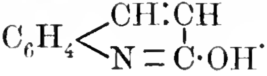
4 : 4′-*Dimethylstilbazole*, $C_{15}H_{15}N$, obtained by the condensation of 2 : 4-lutidine with *p*-tolualdehyde in the presence of zinc chloride at 180—190°, is only sparingly soluble in alcohol, acetone, or benzene and melts at 202°. The *mercurichloride* melts at 160°, the *aurichloride* at 170°, the *platinichloride* at 208°, and the *hydrobromide* at 115°. Its *dihydro*-derivative, $C_{15}H_{17}N$, crystallises from alcohol in glistening, white plates and melts at 103°. The *platinichloride* melts at 168° and the *aurichloride* at 142°.

4 : 4′-*Dimethylstilbazoline*, $C_{15}H_{23}N$, is an oil; its *platinichloride* melts at 104—105°.

4-*Methylpicolyl*-p-*tolylalkine* [*β-hydroxy*-4 : 4′-*dimethyldihydrostilbazole*], $C_{15}H_{17}ON$, is obtained as a by-product in the preparation of 4 : 4′-dimethylstilbazole. It dissolves readily in alcohol and melts at 64°. The *mercurichloride* melts at 197° and the *platinichloride* at 181°.

Phthalic anhydride and 2 : 4-lutidine yield a *phthalone*, $C_{15}H_{11}O_2N$, melting at 262°. Formaldehyde and 2 : 4-lutidine yield 2 : 4-lutidylalkine. J. J. S.

Carbostyril as a By-product in a Molasses Furnace. Edmund O. von Lippmann (*Ber.*, 1905, **38**, 3829—3830).—Three hundred grams of a crystalline sublimate were obtained from a crack in the masonry of a furnace used for the ignition of sugar-liquors. A part of this was soluble in water, but the most important constituent was separated by extracting with alcohol and ether, and after crystallisation from alcohol was found to be carbostyril,



$C_6H_4\Big<\begin{matrix}CH:CH\\ N=C\cdot OH\end{matrix}$. T. M. L.

Condensation of Anthranilic Acid with Ethyl Benzoylacetate. Stefan von Niementowski (*Bull. Acad. Sci. Cracow*, 1905, 285—286).—The condensation of anthranilic acid with ethyl benzoylacetate leads to the formation of various products, depending on the proportions of the interacting substances, the purity of the materials, and the duration and the temperature of the reaction. The chief product is ethyl 4-hydroxy-2-phenylquinoline-3-carboxylate, melting at 262°; at high temperatures, up to 240°, or on prolonged heating, triphenylbenzene is formed. A *substance*, $C_{32}H_{20}O_5N_2$, which resembles the sparingly soluble condensation products of ethyl acetoacetate with anthranilic and *m*-bromoanthranilic acids, benzanilide, a *substance* which resembles and melts a few degrees higher than ethyl 4-hydroxy-2-phenylquinoline-3-carboxylate, and a *derivative* melting at 318° are formed also. G. Y.

Reaction between Nitroquinaldines and Aldehydes. Albert Schmidt (*Ber.*, 1905, **38**, 3715—3723).—8-*Nitro-2-styrylquinoline*, $NO_2\cdot C_9NH_5\cdot CH{:}CHPh$, is obtained when 8-nitroquinaldine and benzaldehyde are heated in an oil-bath at 150° for 4—5 hours. It crystallises from alcohol in pale yellow needles, melts at 142°, and dissolves readily in most organic solvents. The *hydrochloride* crystallises in reddish-yellow, glistening plates, which decompose at about 140° and are completely molten at 172°. The *platinichloride* darkens at 231° and is not melted at 290°; the *aurichloride* forms small, orange needles melting at 233°, and the *mercurichloride* similar needles melting at 224°. When reduced with tin and hydrochloric acid, the base yields 8-*amino-2-β-phenylethylquinoline*,

$$NH_2\cdot C_9NH_5\cdot CH_2\cdot CH_2Ph,$$

which crystallises from dilute alcohol in yellow needles melting at 122°. The *hydrochloride*, $C_{17}H_{16}N_2,2HCl$, crystallises from alcohol in carmine-red needles, begins to decompose at 199°, melts at 211°, and is decomposed by water. The *platinichloride* decomposes at 220°.

8-*Nitro-2-*p-*methylstyrylquinoline*, $NO_2\cdot C_9NH_5\cdot CH{:}CH\cdot C_6H_4Me$, crystallises in pale yellow needles and melts at 145°. The *hydrochloride*, $C_{18}H_{14}O_2N_2,HCl,H_2O$, crystallises in purplish-red plates, is decomposed by water, and melts and decomposes at 179—180°. The *platinichloride* forms golden-yellow needles which begin to decompose at 243°. The *aurichloride* melts at 221° and the *mercurichloride* at 226°. When reduced, the base yields 8-*amino-*2-p-*tolylethylquinoline*, $NH_2\cdot C_9NH_5\cdot CH_2\cdot CH_2\cdot C_6H_4Me$, which crystallises in yellow needles melting at 161°. The *hydrochloride*, $C_{18}H_{18}N_2,2HCl$, crystallises in carmine-red needles and melts at about 222°; the *platinichloride*, $(C_{18}H_{18}N_2)_2,H_2PtCl_6$, decomposes at 230°.

5-*Nitro-2-styrylquinoline* crystallises from dilute alcohol in very long, pale yellow needles melting at 127°. The *hydrochloride* forms golden-yellow needles, which sinter at 204° and melt at 213°. The *platinichloride* begins to decompose at 199°; the *aurichloride* sinters at 218° and melts at 237°; the *mercurichloride* melts indefinitely at about 249—250° and the *picrate* at 236°. The *dibromide*,

$$NO_2\cdot C_9NH_5\cdot CHBr\cdot CHBrPh,$$

crystallises in colourless needles and melts and decomposes at 164°. When reduced, the base yields 5-*amino-2-β-phenylethylquinoline* in the form of yellow needles melting at 185°. The *hydrochloride*,

$$C_{17}H_{16}N_2,2HCl,$$

crystallises in pale red needles, begins to decompose at 229°, and melts at 251°. The *platinichloride* forms minute, golden-brown needles and decomposes at 262°.

5-*Nitro*-2-p-*methylstyrylquinoline* melts at 135°, its *hydrochloride* sinters at 216° and melts at 225°, the *platinichloride* decomposes at 220°, the *mercurichloride* sinters at 244° and melts at 256°, and the *picrate* melts and decomposes at 255°. The *dibromide*, $C_{18}H_{14}O_2N_2Br_2$, crystallises in snow-white needles, becomes yellow at 120°, and then decomposes. When reduced, the base yields 5-*amino*-2-p-*tolylethylquinoline*, $C_{18}H_{18}N_2$, which forms yellow needles melting at 173°; the *hydrochloride* melts at 243°.

6-*Nitro-2-styrylquinoline* forms pale yellow needles, melts at 192°, and is insoluble in water or ether. The *hydrochloride* crystallises in long, pale yellow needles and melts at 205°, the *platinichloride* begins to decompose at 200°, the *aurichloride* melts at 218°, and the *mercurichloride* at about 245° after sintering at 239°. When reduced, the base yields 6-*amino-2-β-phenylethylquinoline*, which melts at 204°. The *hydrochloride* becomes red at 140° and melts at 253°. The *platinichloride* is not molten at 290°, and the *mercurichloride* begins to decompose at 150°.

J. J. S.

Condensation of *o*-Methylquinaldine [2:8-Dimethylquinoline] with Aldehydes.

Martin Hoffmann (*Ber.*, 1905, **38**, 3709—3714).—*Benzylidene*-o-*methylquinaldine* [*2-styryl-8-methylquinoline*],

$$C_9NH_5Me\cdot CH\colon CHPh,$$

obtained by the action of benzaldehyde on 2 : 8-dimethylquinoline (Doebner and von Miller, Abstr., 1884, 184) at 150—155°, crystallises from alcohol in colourless, transparent, hexagonal plates, melting at 72° and soluble in all organic solvents. The *hydrochloride* crystallises in large, yellow needles and melts at 113°. The *mercurichloride* forms golden-yellow, glistening plates melting at 244°; the *platinichloride* melts at 229—230°, the *aurichloride* at 214°, and the *picrate* crystallises from methyl alcohol in small, yellow needles.

2-o-*Nitrostyryl-8-methylquinoline*, $C_{18}H_{14}O_2N_2$, crystallises in felted needles melting at 96°. The *hydrochloride* forms yellow needles, the *mercurichloride* also yellow needles melting above 280°; the *platinichloride* melts at 247°, and the *aurichloride* at 238°.

2-m-*Nitrostyryl-8-methylquinoline* forms a pale yellow powder melting at 109°. The *hydrochloride* melts at 223°, the *mercurichloride* at 249—250°, the *platinichloride* at 269°, and the *aurichloride* melts and decomposes at 209°.

2-p-*Nitrostyryl-8-methylquinoline* forms dark red crystals melting at 112°. The *hydrochloride* melts at 125—126°, the *aurichloride* at 239°, and the *platinichloride* at 264°.

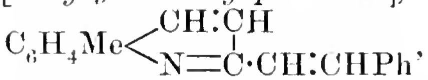
2-*Methylenedioxystyryl-8-methylquinoline*, $C_{19}H_{15}O_2N$, obtained from piperonal and 2 : 8-dimethylquinoline at 120°, crystallises in colourless, glistening plates and melts at 176°. The *hydrochloride* forms yellow needles melting at 244°, and the *picrate* copper-coloured, glistening plates melting at 239—240°. The *mercurichloride, aurichloride*, and *platinichloride* are oils.

Formaldehyde and 2 : 8-dimethylquinoline yield a product with no definite boiling point, but from this a *benzoyl* derivative, $C_{19}H_{17}O_2N$, melting at 118°, has been prepared.

The following salts of 8-*methyl-2-Δ^a-butenylquinoline* have been prepared: *hydrochloride*, yellow crystals melting at 198—199°, *mercurichloride*, colourless needles melting at 212—213°, *aurichloride*, golden-yellow needles melting at 208°. From 8-*methyl*-2-iso*butenylquinoline*, the *hydrochloride* melting at 254°, *aurichloride* at 190—191°, and *picrate* at 164—165° have been obtained. J. J. S.

Condensation of *p*-Methylquinaldine [2:6-Dimethylquinoline] with Aromatic Aldehydes. Georg Gasda (*Ber.*, 1905, **38**, 3699—3704).—2 : 6-Dimethylquinoline (Doebner and von Miller, Abstr., 1884, 184) readily condenses with aromatic aldehydes, especially in the presence of zinc chloride, yielding derivatives of 2-*irazole* [2-*styrylquinoline*],  $C_6H_4<\begin{array}{l}CH{:}CH\\ N{=}\overset{|}{C}\cdot CH{:}CHPh\end{array}$, so called on account of the optical properties of the bases thus formed.

6-*Methyl-2-irazole* [2-*styryl*-6-*methylquinoline*],



$$C_6H_4Me<\begin{array}{l}CH{:}CH\\ N{=}\overset{|}{C}\cdot CH{:}CHPh\end{array},$$

obtained from 2 : 6-dimethylquinoline and benzaldehyde, crystallises from alcohol in large, colourless, strongly refractive prisms melting at 137° and readily soluble in chloroform or acetone. The *hydrochloride* crystallises in microscopic, greenish-yellow needles, becomes brown at 215°, and melts at 243°. The *aurichloride* crystallises from alcohol in golden-yellow needles and melts at 215°; the *platinichloride* decomposes at 279°, the *mercurichloride* melts at 223°, and the *picrate* at 234°. All the salts are practically insoluble in water or ether. The *dibromide*, $C_{18}H_{15}NBr_2$, crystallises from alcohol in colourless plates melting at 169°.

When reduced with sodium and alcohol, the base yields a hexahydro-derivative. 6-*Methyl-2-irazoline*, $C_{18}H_{21}N$, which crystallises in colourless needles melting at 66°, distils at 254° under 25 mm. pressure and dissolves in most organic solvents. The *hydrochloride* is hygroscopic, crystallises in small, colourless needles, sinters at 202°, and melts at 209—210°. The *benzoyl* derivative melts at 102°.

2-m-*Nitrostyryl*-6-*methylquinoline*, $C_9NH_5Me\cdot CH{:}CH\cdot C_6H_4\cdot NO_2$, obtained from 6-methylquinaldine and *m*-nitrobenzaldehyde, crystallises from alcohol in short, yellow prisms melting at 201°, and is not readily soluble in the ordinary organic solvents. The *hydrochloride* becomes brown at 257°, the *platinichloride* crystallises in orange-coloured needles and is not decomposed at 300°, the *mercurichloride* melts at 254° and dissolves in hydrochloric acid and alcohol, the *picrate* melts at 271°, and the *dibromide* becomes brown at 205° and melts at 209°.

2-p-*Hydroxystyryl*-6-*methylquinoline* crystallises in glistening needles, melts at 249°, and is only sparingly soluble in water or ether. The *hydrochloride* crystallises in brick-red needles, dissolves in water, alcohol, or hydrochloric acid, and is not decomposed at 300°. The *platinichloride* becomes brown at 249°, the *mercurichloride* melts at 262°, the *picrate* at 251°, and the *dibromide* at 265—266°, after darkening at 255°.

The corresponding *hexahydro*-derivative, $C_{18}H_{21}ON$, crystallises from alcohol in glistening needles, melts at 101—102°, and dissolves readily in most organic solvents. The *hydrochloride* forms pale yellow needles and melts at 257°; the *picrate* melts at 271° and is readily soluble in water or alcohol.

2-*p*-*Methylstyryl-6-methylquinoline* forms large, colourless, strongly refractive needles and melts at 144°; the *hydrochloride* forms yellow needles, sinters at 230°, and melts at 251°; the *aurichloride* crystallises in golden-red needles, melts at 227°, and is sparingly soluble in alcohol. The *platinichloride* melts at 282°, the *mercurichloride* at 209—210°, and the *dibromide* at 167°.

The corresponding *hexahydro*-derivative melts at 68°, its *hydrochloride* at 232°, its *platinichloride* at 224°, and its *benzoyl* derivative at 75°. J. J. S.

Constitution of Cyanine Dyes. Gilbert Book (*Ber.*, 1905, **38**, 3804—3806).—The colour of ethyl-red is retained by its di-iodide, because, although the unsaturated linking between the two quinoline groups disappears, one of them retains a quinonoid structure.

When 2 : 4-dimethylquinolinium methiodide is acted on by alcoholic potash, no change in colour is observed when the solution is kept in a corked flask or in a current of hydrogen; the appearance of the colour and the formation of the dye are due to atmospheric oxidation, and the process is thus entirely distinct from that which gives rise to the cyanine dyes. T. M. L.

***iso*Quinoline Derivatives from 4-Methylphthalic Acid.** Waldemar Findeklee (*Ber.*, 1905, **38**, 3542—3553).—The acid was prepared from *m*-toluidine, which was converted into *m*-toluonitrile, nitrated in the para-position, reduced, diazotised, and converted into dicyanotoluene, which was hydrolysed to 4-methylphthalic acid. Particulars are given of the methods adopted and the properties of the intermediate products.

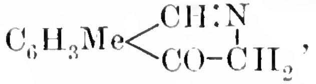
4-*Methylphthaliminoglycine ester*, $C_6H_3Me\langle\begin{smallmatrix}CO\\CO\end{smallmatrix}\rangle N\cdot CH_2\cdot CO_2Et$, prepared by the action of ethyl chloroacetate on potassium methylphthalimide, crystallises from hot water and melts at 97°.

The free *acid* is best prepared by heating methylphthalic anhydride with glycine; it crystallises from hot water in colourless needles and melts at 193—194°; the *silver* salt forms a white precipitate and the *copper* salt minute, felted needles; the acid prepared by this method may be used conveniently as a source of the ester.

By the action of sodium methoxide, the ester is caused to undergo isomeric change, the ethyl group at the same time being replaced by methyl. *Methyl 4-oxy-7-methylisocarbostyril-3-carboxylate*,

$$C_6H_3Me\Big\langle\begin{matrix}CO\cdot NH\\ \quad\ \ |\\ CO\cdot CH\cdot CO_2Me\end{matrix},$$

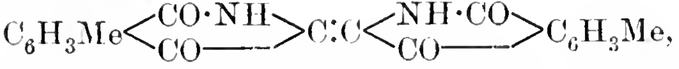
crystallises from methyl alcohol in colourless needles and melts at 210° to a dark liquid; the dilute alcoholic solution shows a violet-blue fluorescence. 4-*Oxy-7-methyl*iso*carbostyril*, $C_6H_3Me{<}\begin{smallmatrix}CO\cdot NH\\ \vert\\ CO\cdot CH_2\end{smallmatrix}$, prepared by heating the ester with 50 per cent. sulphuric acid, separates from hot water, acetone, or alcohol in red crystals. Phosphorus oxychloride converts it into 1-*chloro-4-oxy-7-methyl*iso*quinoline*, $C_6H_3Me{<}\begin{smallmatrix}CCl{:}N\\ \vert\\ CO\ \ CH\end{smallmatrix}$, which crystallises from acetic acid and is reduced by hydriodic acid at 180° to 4-*oxy-7-methyl*iso*quinoline*,



$$C_6H_3Me{<}\begin{smallmatrix}CH{:}N\\ \vert\\ CO{-}CH_2\end{smallmatrix},$$

which crystallises from hot water in minute, felted needles and melts at 162°. 1-*Chloro-7-methyl*iso*quinoline*, $C_6H_3Me{<}\begin{smallmatrix}CCl{:}N\\ \vert\\ CH{:}CH\end{smallmatrix}$, prepared by the action of phosphorus oxychloride on the preceding compound, is a yellow oil, which gives a *picrate* melting at 141°. It is reduced by phosphorus and hydriodic acid to 7-*methyl*iso*quinoline*, C_9NH_6Me, which solidifies to a white mass, melts at 66°, and has a characteristic odour resembling that of *iso*quinoline; the *picrate* melts at 197°, the *chromate* at 126°, the *platinichloride* with decomposition at 225°. The compound differs widely from 6-methyl*iso*quinoline, and the alternative formulæ corresponding with the latter position of the methyl group are therefore excluded.

Dimethylcarbindigotin,



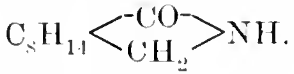
$$C_6H_3Me{<}\begin{smallmatrix}CO\cdot NH\\ CO{-\!-\!-}\end{smallmatrix}{>}C{:}C{<}\begin{smallmatrix}NH\cdot CO\\ CO{-\!-\!-}\end{smallmatrix}{>}C_6H_3Me,$$

prepared by atmospheric oxidation or by the action of chromic acid on 4-oxy-7-methyl*iso*carbostyril, crystallises from nitrobenzene in small, reddish-brown needles with a green, metallic lustre.

7-*Methylphthalonimide*, $C_6H_3Me{<}\begin{smallmatrix}CO\cdot NH\\ \vert\\ CO\cdot CO\end{smallmatrix}$, prepared by oxidising the oxy*iso*carbostyril with fuming nitric acid, crystallises from 50 per cent. alcohol in feathery needles and melts at 213°. It is hydrolysed by alkalis to *methylphthalonamic acid*, $NH_2\cdot CO\cdot C_6H_3Me\cdot CO\cdot CO_2H$, which is converted by hypochlorites into 6-*methylisatin*, which crystallises from hot water in red needles, melts at 169°, gives the indophenine reaction, and is isomeric with Meyer's *p*-methylisatin (Abstr., 1884, 47).

Methylphthalonic acid, $CO_2H\cdot C_6H_3Me\cdot CO\cdot CO_2H$ [1 : 4 : 2], prepared from methylphthalonimide by the action of concentrated hydrochloric acid, separates from hot water in colourless crystals and melts at 103°; the insoluble *silver* salt was analysed. The *phenylhydrazone*, $C_{16}H_{14}O_4N_2$ [or possibly its anhydride, $C_{16}H_{12}O_3N_2$], prepared by the action of phenylhydrazine hydrochloride on the acid, crystallises in yellow needles and melts with frothing at 213°. T. M. L.

The Camphidones. JULIUS TAFEL and HEINRICH BUBLITZ (*Ber.*, 1905, **38**, 3806—3812).—*a*-Camphidone has been converted through the nitroso-compound into a campholide identical with that obtained by Baeyer and Villiger (Abstr., 1900, i, 133) by oxidising camphor with persulphuric acid. If, therefore, camphor and the campholide are written $C_8H_{14}<\substack{CH_2\\|\\CO}$ and $C_8H_{14}<\substack{CH_2\text{-}\\\text{-}CO\text{-}}>O$, *a* camphidone has the formula $C_8H_{14}<\substack{CH_2\text{-}\\\text{-}CO\text{-}}>NH$, and *β*-camphidone the formula



$$C_8H_{14}<\substack{\text{-}CO\text{-}\\CH_2}>NH.$$

Nitroso-a-camphidone, $C_8H_{14}<\substack{CH_2\text{-}\\\text{-}CO\text{-}}>N{\cdot}NO$, crystallises from light petroleum, melts at 127°, and is considerably more stable than nitrosopyrrolidone, although it decomposes when distilled. Boiling potassium hydroxide converts it into an *acid*, probably $CH_2{:}C_8H_{14}{\cdot}CO_2H$, which melts at 149—155°, and when the latter is distilled it is converted into a campholide identical with that derived from camphor; in each case the crude substance appears to be a mixture, probably with a polymeric lactone, but identical products were obtained by crystallising from concentrated hydriodic acid.

Nitroso-β-camphidone, $C_8H_{14}<\substack{\text{-}CO\text{-}\\CH_2}>N{\cdot}NO$, crystallises from light petroleum in long, glistening, yellow needles and melts at 158°. It is about as stable as the *a*-isomeride, and, when decomposed by potassium hydroxide, yields a similar mixed campholide, from which, however, none of Baeyer and Villiger's product could be isolated.

Di-β-camphidone anhydride, $C_{20}H_{32}ON_2$, prepared by heating *β*-camphidone with phosphorus oxychloride, melts at 144—145°, has $[a]_D + 207{\cdot}4°$ in benzene at 20°, dissolves readily in organic solvents and in mineral acids, but is reprecipitated from the latter by sodium acetate; the yield is good, and as *a*-camphidone does not give an anhydride, the use of phosphorus oxychloride affords a convenient method of separating the isomerides. When dissolved in acetic acid, the anhydride readily yields a *bromide* which crystallises from acetic acid in orange-yellow scales, melts at 196°, and is decomposed again by the action of acetone.

T. M. L.

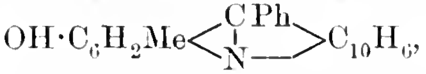
Syntheses of Aminonaphthacridines. Fritz Ullmann and Emil Bühler (*Zeit. Farb. Text. Ind.*, 1905, **4**, 521—522. Compare Ullmann and Naef, Abstr., 1900, i, 361; Ullmann and Torre, Abstr., 1904, i, 929).—9-Amino-1 : 2-phenonaphthacridine has been prepared by the following methods. The percentages given are the relation of the yield obtained to the theoretical. (1) A mixture of *m*-tolylenediamine hydrochloride, sulphur, and *β*-naphthol is heated at 180—190° (19·4 per cent.). (2) Dihydroxydinaphthyl disulphide and *m*-tolylenediamine are heated with *β*-naphthol at 180—190° (20 per cent.). (3) Anhydroformaldehyde-*m*-phenylenediamine is treated with *β*-naphthol (10·7 per cent.). (4) *β*-Naphthol, *m*-phenylenediamine, and trioxymethylene are fused together and the product distilled rapidly (24·4 per cent.). (5) *β*-Naphthol and *m*-phenylenediamine are heated with dihydroxydinaphthylmethane (18·6 per cent.).

The orange-yellow, aqueous solution of 9-amino-1 : 2-phenonaphthacridine dyes tannin mordanted cotton-wool clear orange-yellow shades;

the *nitrate*, $C_{17}H_{12}N_2,HNO_3$, crystallises in red needles and is less soluble than the hydrochloride in water.

Dihydroxydinaphthyl disulphide is obtained in a yield of 88·1 per cent. of the theoretical when lead oxide is added to a solution of β-naphthol and sulphur in nitrobenzene at 160—170°. G. Y.

Hydroxyacridines. FRITZ ULLMANN and ROBERT FITZENKAM (*Ber.*, 1905, **38**, 3787—3796. Compare Ullmann, Racovitza, and Rozenband, Abstr., 1902, i, 240; Ullmann, Rozenband, Mühlhauser, and Grether, *ibid.*; Ullmann and Grether, Abstr., 1903, i, 447).—10-*Hydroxy-7-phenyl-9-methylpheno-aβ-naphthacridine*,

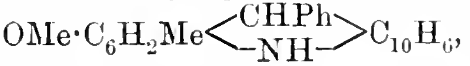


$$OH\cdot C_6H_2Me<\overset{CPh}{\underset{N}{|}}>C_{10}H_6,$$

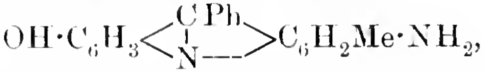
is formed by heating 9-amino-12-phenyl-10-methylpheno-aβ-naphthacridine with 10 per cent. sulphuric acid at 200—210° under pressure for eight hours, or, together with its leuco-base, by warming *p*-amino-*o*-cresol with benzaldehyde and heating the resulting benzylidene compound with β-naphthol at 210—220°. It crystallises from aniline or nitrobenzene in yellowish-brown needles, melts above 360°, and dissolves in alcoholic hydrogen chloride to form a brownish-red solution, in alcoholic sodium hydroxide to form a yellow solution, or in concentrated sulphuric acid to form a yellowish-brown solution with dark green fluorescence; the base is precipitated on dilution of its solution in glacial acetic acid; the *hydrochloride* forms steel-blue, glistening needles and melts and decomposes at about 330°.

The *leuco-base* is obtained as a slightly yellowish-brown powder, which does not melt at 350°; it is oxidised to the phenonaphthacridine by ferric chloride in acetic acid solution.

p-Nitro-*o*-cresol is best prepared by diazotising nitrotoluidine in 10 per cent. sulphuric acid at 0° and pouring the product into boiling dilute sulphuric acid. When shaken with methyl sulphate and aqueous sodium hydroxide, it forms the *methyl ether*, $OMe\cdot C_6H_3Me\cdot NO_2$, which crystallises in yellow needles, melts at 71°, and on reduction with stannous chloride and alcoholic hydrochloric acid yields the *stannichloride*, $(C_8H_{11}ON)_2,2HCl,SnCl_4$, crystallising in colourless needles. The free *base*, $NH_2\cdot C_6H_3Me\cdot OMe$, crystallises in long needles, melts at 55°, and boils at 250—252°. The *hydrochloride*, $C_8H_{11}ON,HCl$, crystallises in glistening, almost colourless needles and melts at 269—270°. The *acetyl* derivative, $C_8H_{10}ONAc$, crystallises in small, colourless leaflets and melts at 132°.

When heated with benzaldehyde and β-naphthol at 220°, *p*-amino-*o*-cresol methyl ether forms 10-*methoxy-7-phenyl-9-methyl-7:12-dihydropheno-aβ-naphthacridine*,  $OMe\cdot C_6H_2Me<\overset{CHPh}{\underset{NH}{}}>C_{10}H_6$, which is obtained as a colourless, crystalline powder, melts at 232—234°, and forms colourless solutions with blue fluorescence. 10-*Methoxy-7-phenyl-9-methylpheno-aβ-naphthacridine*, $C_{25}H_{19}ON$, is obtained at the same time, and it is also formed by oxidation of the leuco-base with ferric chloride in acetic acid solution, or with bromine in carbon tetrachloride solution; it crystallises in glistening, yellow leaflets, melts at 205—206°, and dissolves in dilute acids or organic solvents to form yellow solutions with bluish-green fluorescence. The *picrate* forms a yellow, crystalline powder; the *nitrate*, $C_{25}H_{19}ON,HNO_3$, crystallises in golden prisms and melts at 224°.

2-Amino-8-hydroxy-5-phenyl-3-methylacridine,



$$\mathrm{OH\cdot C_6H_3}<\!\begin{matrix}\mathrm{CPh}\\ |\\ \mathrm{N}\end{matrix}\!>\mathrm{C_6H_2Me\cdot NH_2},$$

is formed together with the dihydroacridine when phenyltetra-aminoditolylmethane is heated with resorcinol at 165—185°, or by oxidation of the leuco-base with ferric chloride. It crystallises from aniline or alcohol in glistening, orange needles, melts at 368—373°, and dissolves in dilute sodium hydroxide, dilute acids, or concentrated sulphuric or glacial acetic acid, forming yellow solutions with green fluorescence. The *hydrochloride* forms yellowish-brown crystals and is dissociated by water; the *acetate*, $C_{20}H_{16}ON_2,C_2H_4O_2$, crystallises in glistening, orange, hygroscopic needles, melts and decomposes at 187—193°, and in aqueous solution dyes tannin mordanted cotton-wool yellow. The *leuco-base*, $C_{20}H_{18}ON_2$, forms an almost colourless powder, melts at 305—311°, and dissolves in alcohol containing traces of an alkali hydroxide.

2 : 8-*Dihydroxy*-3 : 7-*dimethylacridine*,

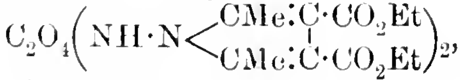
$$\mathrm{OH\cdot C_6H_2Me}<\!\begin{matrix}\mathrm{CH}\\ |\\ \mathrm{N}\end{matrix}\!>\mathrm{C_6H_2Me\cdot OH},$$

is formed by heating tetra-aminoditolylmethane with sulphuric acid at 220° under pressure. It crystallises from nitrobenzene in small, yellowish-brown needles and melts above 360°; the *sodium* derivative, $C_{15}H_{12}O_2NNa$, crystallises in orange needles and dissolves in water or alcohol to form yellow solutions with green fluorescence. The *diacetyl* derivative, $C_{19}H_{17}O_4N$, crystallises in glistening prisms, melts at 202°, and is hydrolysed by dilute acids or alkali hydroxides. The *dibenzoyl* derivative, $C_{29}H_{21}O_4N$, crystallises in yellow leaflets, melts at 258°, and forms the *hydrochloride*, $C_{29}H_{21}O_4N,HCl$, crystallising in yellow needles and melting at 280—285°. G. Y.

Coloured and Colourless Di-imines. FRIEDRICH KEHRMANN (*Ber.*, 1905, **38**, 3777—3778. Compare Willstätter and Pfannenstiel, Abstr., 1905, i, 669; Pringsheim, *ibid.*, i, 934).—The author considers that there is no evidence to support the suggestion that there are two series of quinonedi-imine salts, but that many of the deeply-coloured oxidation derivatives of amines are of the nature of quinhydrones.

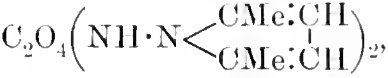
G. Y.

Condensation Products of Oxalylhydrazide. I. CARL BÜLOW (*Ber.*, 1905, **38**, 3914—3917. Compare Abstr., 1903, i, 196; Bülow, Riess, and Sautermeister, Abstr., 1905, i, 660).—*Ethyl* 1-*oxamidobis*-2 : 5-*dimethylpyrrole*-3 : 4-*dicarboxylate*,



$$\mathrm{C_2O_4}\left(\mathrm{NH\cdot N}<\!\begin{matrix}\mathrm{CMe{:}C\cdot CO_2Et}\\ |\\ \mathrm{CMe{:}C\cdot CO_2Et}\end{matrix}\right)_2,$$

is formed by the condensation of oxalylhydrazide (Curtius, Schöfer, and

Schwan, Abstr., 1895, i, 264) with ethyl diacetylsuccinate in boiling acetic acid solution. It crystallises in leaflets, melts at 291—293°, is soluble in boiling nitrobenzene, dissolves without change in dilute alkali hydroxides or aqueous ammonia, from which it is precipitated by the action of carbon dioxide, and separates unchanged from its solution in concentrated sulphuric acid when poured on to ice. When heated above its melting point, the *acid* obtained on hydrolysis of the ester yields 1-*oxamidobis*-2 : 5-*dimethylpyrrole*,  $C_2O_4\left(NH\cdot N<\begin{matrix}CMe:CH\\ |\\ CMe:CH\end{matrix}\right)_2$, which is formed also by the condensation of oxalylhydrazide with acetonylacetone in glacial acetic acid solution. It crystallises in glistening, white leaflets, dissolves readily in boiling alcohol, acetone, or dilute alkali hydroxides, is precipitated by carbon dioxide from its alkaline solution, and gives the pine-wood and Laubenheimer's pyrrole reactions. G. Y.

Action of 2 : 5-Dimethylpyrazine on Aldehydes. R. FRANKE (*Ber.*, 1905, **38**, 3724—3728).—2-*Styryl*-5-*methylpyrazine*, $C_{13}H_{12}N_2$, and 2 : 5-*distyrylpyrazine*, $C_{20}H_{16}N_2$, obtained by the condensation of 2 : 5-dimethylpyrazine and benzaldehyde with zinc chloride at 200°, may be separated by distillation with steam. Styrylmethylpyrazine distils over slowly, and after several crystallisations from alcohol forms colourless, glistening plates melting at 90°, and yields a *picrate*, $C_{19}H_{15}O_7N_5,4H_2O$, melting at about 132°. Distyrylpyrazine is not volatile with steam, and crystallises from a mixture of benzene and light petroleum in sulphur-yellow, glistening plates melting at 219°. The *hydrochloride*, $C_{20}H_{16}N_2,HCl$, forms red crystals; the *platinichloride* also forms reddish-yellow crystals and melts at 219°. The *picrate* is unstable and melts at 165°. Attempts to reduce the distyryl derivative were not successful.

2 : 5-*Di*-γγγ-*trichloropropenylpyrazine*, obtained by the action of chloral on dimethylpyrazine at the ordinary temperature, crystallises with $4H_2O$ in compact prisms, melts at 89°, and dissolves readily in alcohol.

Di-p-*methylstyrylpyrazine*, $C_{22}H_{20}N_2$, obtained from 2 : 5-dimethylpyrazine, *p*-tolualdehyde, and zinc chloride at 170° in an oil-bath, crystallises from benzene and melts at 238°. The *hydrochloride*, $C_{24}H_{20}N_2,HCl,\frac{1}{2}H_2O$, crystallises in small, pale red needles, becomes yellow at 160°, and melts at 240°. The *mercurichloride*,

$$(C_{22}H_{20}N_2)_2HgCl_2,$$

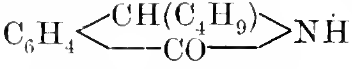
melts at 231° and the *platinichloride* at 206°.

Di-p-*methoxystyrylpyrazine*, $C_{22}H_{20}O_2N_2$, crystallises from benzene or chloroform in yellow plates and melts at 235°. The *mercurichloride*, $C_{22}H_{20}O_2N_2,HCl,HgCl_2,3H_2O$, melts at 96°. The *picrate* crystallises from chloroform in bright red crystals, $C_{22}H_{20}O_2N_2,C_6H_3O_7N_3,2CHCl_3$, melting at 217°.

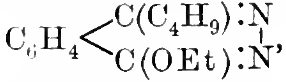
2-o-*Hydroxystyryl*-5-*methylpyrazine*, $C_{13}H_{12}ON_2$, obtained from dimethylpyrazine, salicylaldehyde, and zinc chloride at 170—180°, melts at 228° and dissolves readily in alcohol and glacial acetic acid; the *picrate* melts at 227°.

2-p-*Nitrostyryl*-5-*methylpyrazine*, $C_{13}H_{11}O_2N_3$, forms a yellow powder melting at about 174°. The *platinichloride* decomposes at about 200°. J. J. S.

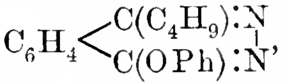
Condensation of Ethyl Acetoacetate with Phenylmethylpyrazolone. ROBERT STOLLÉ (*Ber.*, 1905, **38**, 3856. Compare Abstr., 1905, i, 838).—The lactone constitutional formula ascribed to the condensation product of ethyl acetoacetate and phenylmethylpyrazolone has already been put forward by G. Cohn [Tabular summary of the Pyrazole derivatives]. E. F. A.

1-*iso*Butylphthalazine. HANS WÖLBLING (*Ber.*, 1905, **38**, 3925—3928).—When reduced with zinc and fuming hydrochloric acid, 1-*iso*butylphthalazone (Bromberg, Abstr., 1896, i, 579) yields 1-iso*butylphthalimidine*,  $C_6H_4<\begin{array}{c}CH(C_4H_9)\\CO\end{array}>NH$, which forms colourless, glistening crystals and melts at 153°.

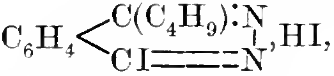
On slow evaporation of its ethereal solution, 4-chloro-1-*iso*butylphthalazine (Bromberg, *loc. cit.*) crystallises in transparent, doubly-refracting needles melting at 38°. When boiled with sodium ethoxide in alcoholic solution, it forms *4-ethoxy-*1-iso*butylphthalazine*,



$$C_6H_4<\begin{array}{l}C(C_4H_9):N\\C(OEt):N\end{array},$$

which is obtained as an oil having an odour of hyacinths; the *sulphate*, $(C_{14}H_{18}ON_2)_2,H_2SO_4$, crystallises from alcohol and melts at 109°. 4-*Phenoxy*-1-iso*butylphthalazine*,  $C_6H_4<\begin{array}{l}C(C_4H_9):N\\C(OPh):N\end{array}$, formed by heating 4-chloro-1-*iso*butyl*phthalazine* with sodium phenoxide in phenol, crystallises in white needles and melts at 108°.

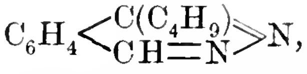
When warmed with hydriodic acid of sp. gr. 1·70, 4-chloro-1-*iso*butylphthalazine yields 4-*iodo*-1-iso*butylphthalazine hydriodide*,



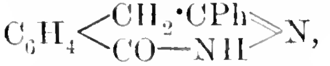
$$C_6H_4<\begin{array}{l}C(C_4H_9):N\\CI=\!=\!=N\end{array},HI,$$

which crystallises in glistening, orange, doubly-refracting needles and melts at 127°.

The action of boiling hydriodic acid of sp. gr. 1·70, in presence of red phosphorus, on 4-chloro-1-*iso*butylphthalazine leads to the formation of 1-*iso*butylphthalazine, ammonia, *iso*butylphthalazone, and *iso*butyldihydro*iso*indole.

1-iso*Butylphthalazine*,  $C_6H_4<\begin{array}{l}C(C_4H_9)\\CH=N\end{array}>N$, is obtained as an oil which is soluble in mineral acids; the *platinichloride*, $(C_{12}H_{14}N_2)_2,H_2PtCl_6$, melts at 157°; the *hydriodide* crystallises in brown leaflets and decomposes at about 100°; the *aurichloride* crystallises in yellow needles, melts at 137°, and decomposes at about 183°; the *dichromate*, $(C_{12}H_{14}N_2)_2,H_2Cr_2O_7$, is obtained as a red, crystalline precipitate; the *ferrocyanide*, $(C_{12}H_{14}N_2)_2,H_4Fe(CN)_6$, forms a yellow, voluminous precipitate and decomposes at high temperatures without melting. G. Y.

Action of Hydrazine on β-Deoxybenzoin-*o*-carboxylic Acid and on its Lactone (3-Phenyl*iso*coumarin). Hans Wölbling (*Ber.*, 1905, **38**, 3845—3853).—The *hydrazone anhydride*,

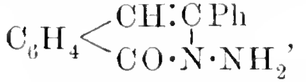


$$C_6H_4<\begin{array}{l}CH_2\cdot CPh\\CO—NH\end{array}>N,$$

prepared by the action of hydrazine hydrate on β-deoxybenzoin-*o*-carboxylic acid, crystallises in long, colourless needles melting at 202°. The *methyl* derivative,

$C_6H_4<\begin{array}{l}CH_2\cdot CPh\\CO\cdot NMe\end{array}>N$, crystallises in long, colourless, glistening, asbestos-like needles melting at 133°; the corresponding *ethyl* derivative forms colourless needles melting at 142°.

The *nitroso*-derivative, $C_{15}H_{11}O_2N_3$, separates in clear, doubly-refracting crystals which melt and decompose at 110°. On reduction with zinc and hydrochloric acid, the hydrazone anhydride is converted into *iso*benzylidenephthalimidine. On warming it with phosphorus oxychloride, an isomeride, 2-*amino*-3-*phenyl*iso*carbostyril*,



$$C_6H_4<\begin{array}{l}CH:CPh\\CO\cdot N\cdot NH_2\end{array},$$

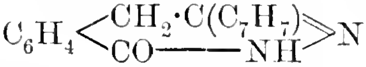
is formed, crystallising in brown, monoclinic leaflets melting at 131°. The nitroso-derivative, crystallising in needles which sinter at 230° and melt at 240°, proved to be identical with nitro*iso*benzylidenephthalimidine. On condensation with benzaldehyde, 2-*benzylideneamino*-3-*phenyl*iso*carbostyril*,

$C_6H_4<\begin{array}{l}CH:CPh\\CO\cdot N\cdot N:CHPh\end{array}$, is formed, which separates in green crystals melting at 116° to a bright green liquid.

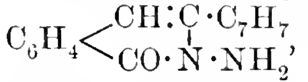
By the interaction of deoxybenzoincarboxylic acid and hydrazine in presence of a large excess of an alkali hydroxide, a *compound* $C_{30}H_{24}O_4N_2$ is formed, which crystallises in doubly-refracting, microscopic, citron-yellow needles and melts at 226°; this forms a dibasic *silver* salt. E. F. A.

Action of Hydrazine on *m*-Tolyl*iso*coumarin. Albert Lieck (*Ber.*, 1905, **38**, 3853—3856).—m-*Methylstilbene*-o-*carboxylic acid*, $C_7H_7\cdot CH:CH\cdot C_6H_4\cdot CO_2H$, is obtained from *m*-xylidenephthalide by conversion first into *m*-methyldeoxybenzoincarboxylic acid, reduction of this by sodium amalgam, and dehydration of the hydroxy-acid so obtained by heating for one hour at 215°. It crystallises in thin, yellowish-white leaflets melting at 158°; the *silver* salt forms a voluminous, colourless precipitate.

By the action of hydrazine hydrate on *m*-tolyl*iso*coumarin a *hydrazone anhydride*,



$C_6H_4<\begin{array}{l}CH_2\cdot C(C_7H_7)\\CO——NH\end{array}>N$, is formed, crystallising in snow-white, obliquely cut plates which sinter at 175° and melt from 190—191°. On heating with 20 per cent. hydrochloric acid, it is converted into an isomeride, 2-*amino*-3-m-*tolyl*iso*carbostyril*,



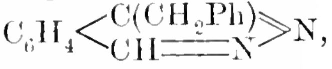
$$C_6H_4<\begin{array}{l}CH:C\cdot C_7H_7\\CO\cdot N\cdot NH_2\end{array},$$

which forms colourless crystals melting at 98—99°. This condensation could not be effected by using phosphorus oxychloride (compare

Wölbling, preceding abstract), nor will methyl *iso*coumarin undergo the hydrazone anhydride condensation. E. F. A.

Phthalazines. ALBERT LIECK (*Ber.*, 1905, **38**, 3918—3924).—4-*Iodo*-1-*benzylphthalazine*, $C_{15}H_{11}N_2I$, is formed by heating 4-chloro-1-benzylphthalazine (Gabriel and Neumann, Abstr., 1893, i, 346) with hydriodic acid boiling at 127°; it crystallises in long, white needles, becomes yellow at 100°, and finally reddish-brown at 146°, when it melts and decomposes.

Prolonged action of hydriodic acid on 4-chloro-1-benzylphthalazine in presence of red phosphorus leads to the formation of 1-*benzylphthalazine hydriodide*, $C_{15}H_{12}N_2,HI$, which crystallises in yellow, rhombic leaflets and decomposes at 100°. The *base*,



$$C_6H_4{<}\begin{matrix}C(CH_2Ph)\\CH{=\!=\!=}N\end{matrix}{>}N,$$

crystallises in white, rectangular plates and melts at 81—82°. The *picrate*, $C_{15}H_{12}N_2,C_6H_3O_7N_3$, crystallises in yellow needles and melts at 146°; the *platinichloride* forms a yellowish-brown, crystalline mass.

When warmed with aniline, 4-chloro-1-benzylphthalazine forms 4-*anilino*-1-*benzylphthalazine*, $C_{21}H_{17}N_3$, which crystallises in white hexahedra and melts at 180°.

Oxidation of 1-benzylphthalazine with potassium permanganate in alkaline solution leads to the formation of 1-*benzoylphthalazine*, $C_8H_5N_2Bz$, which crystallises in matted, white needles, melts at 123—124°, and is readily soluble in the ordinary organic solvents; the yellow, crystalline *platinichloride*, $(C_{15}H_{10}ON_2)_2,H_2PtCl_6$, melts and decomposes at 258°. The *oxime*, $C_8H_5N_2{\cdot}CPh{:}NOH$, crystallises in sheaves of white prisms, melts to a reddish-brown liquid at 243—244°, and is readily soluble in dilute sodium hydroxide or hydrochloric acid, separating from its solution in the latter as the *hydrochloride* in delicate, white needles.

When reduced with sodium amalgam, 1-benzylphthalazine yields 1-*benzyltetrahydrophthalazine*, $C_{15}H_{16}N_2$, which is obtained as an oil; the *hydrochloride*, $C_{15}H_{16}N_2,HCl$, decomposes at 190—200°, is easily soluble in hot water or dilute hydrochloric acid, and reduces Fehling's solution and mercuric oxide; the crystalline *platinichloride*,

$$(C_{15}H_{16}N_2)_2,H_2PtCl_6,$$

commences to decompose at 180°. The *dibenzoyl* derivative,

$$C_{15}H_{14}N_2Bz_2,$$

crystallises in long, yellow plates and melts at 135—136°.

4-*Chloro*-1-*phenylphthalazine*, $C_{14}H_9N_2Cl$, formed by the action of phosphorus oxychloride on 1-phenylphthalazone, crystallises in glistening, white leaflets, melts at 160—161°, is readily soluble in warm xylene, alcohol, toluene, or glacial acetic acid, and when heated with hydriodic acid, boiling at 127°, yields 4-*iodo*-1-*phenylphthalazine*, $C_{14}H_9N_2I$, which crystallises from alcohol in matted, long, white needles, becomes yellow at 120°, and melts and decomposes at 188—189°. When boiled with hydriodic acid and red phosphorus in a reflux apparatus, 4-chloro-1-phenylphthalazine yields 1-*phenylphthalazine hydriodide*, which separates in yellow needles and decomposes at 170—180°. The *base*, $C_{14}H_{10}N_2$, crystallises in white prisms, melts at

142—143°, and is easily soluble in most organic solvents; the *platinichloride* forms orange-yellow crystals and melts and decomposes at 223°; the yellow, crystalline *picrate*, $C_{20}H_{13}O_7N_5$, melts at 180°.

4-*Anilino*-1-*phenylphthalazine*, $C_{20}H_{15}N_3$, obtained by warming 4-chloro-1-phenylphthalazine with aniline, crystallises in needles and melts at 231°.

1-*Phenyltetrahydrophthalazine* is obtained on reduction of 4-chloro-1-phenylphthalazine with sodium amalgam as an almost colourless, aromatic syrup, which distils slowly in a current of steam; the *hydrochloride*, $C_{14}H_{14}N_2,HCl$, forms white needles, commences to decompose at 220°, is melted at 250°, and reduces Fehling's solution and mercuric oxide; the *picrate* is obtained as a yellow emulsion which crystallises when rubbed; the *platinichloride*, $(C_{14}H_{14}N_2)_2,H_2PtCl_6$, crystallises in leaflets and decomposes at 140°. The *dibenzoyl* derivative, $C_{28}H_{22}O_2N_2$, crystallises in long, slightly yellow prisms and melts at 158—159°.

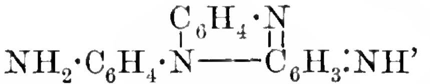
G. Y.

New Mode of Formation of Di-*p*-aminodiphenylamine.

Philippe Barbier and **Paul Sisley** (*Bull. Soc. chim.*, 1905, [iii], **33**, 1232—1234. Compare following abstract).—*p*-Aminoazobenzene hydrochloride is added to a saturated solution of sulphur dioxide in water, and to this zinc dust is gradually added until complete decolorisation is effected. The liquid is then poured into excess of sulphuric acid, diluted with its own volume of water, and the mixture boiled. On cooling, crystals of di-*p*-aminodiphenylamine sulphate separate. From this the base may be liberated with sodium carbonate. It crystallises from boiling water in small needles with a violet tint and melts at 157—158°.

The aminoazo-derivative of *o*-toluidine can be converted by the same method into the corresponding di-*p*-amino-base. T. A. H.

s- and *as*-Phenosafranines.

Philippe Barbier and **Paul Sisley** (*Bull. Soc. chim.*, 1905, [iii], **33**, 1190—1198. Compare Abstr., 1905, i, 840).—Commercial phenosafranine, prepared by oxidising a mixture of 2:4′-diaminodiphenylamine and aniline, contains *s*-phenosafranine,  $NH_2\cdot C_6H_3{<}\genfrac{}{}{0pt}{}{N}{NPh}{>}C_6H_3{:}NH$, which it is proposed to name *indophenosafranine*, and *as*-phenosafranine,  $\begin{array}{l}\quad\quad\quad\quad\quad C_6H_4\cdot N\\ NH_2\cdot C_6H_4\cdot N\text{——}C_6H_3{:}NH\end{array}$, which it is proposed to call *azophenosafranine*. The former was prepared from commercial safranine by repeated crystallisation from dilute hydrochloric acid, the hydrochloride of the *as*-isomeride being the less soluble. *s*-Phenosafranine was prepared by oxidising a mixture of di-*p*-aminodiphenylamine (1 mol.) with aniline (1 mol.), and was purified by repeated crystallisation of the hydrochloride from dilute hydrochloric acid.

Azophenosafranine hydrochloride, $C_{18}H_{15}N_4Cl,3H_2O$, crystallises in dull green lamellæ which exhibit little or no metallic lustre; it becomes anhydrous at 120—130°, and in this state is hygroscopic. One litre of water dissolves 12·88 grams of the salt at 24°. The *free base* may be obtained by adding sodium hydroxide to an aqueous solution of the hydrochloride; it separates from water in small, green crystals, which are heavier than those of indophenosafranine. A litre of water dissolves 0·58 gram and a litre of alcohol (90°) 18·08 grams of the base at 20°.

Indophenosafranine hydrochloride, $C_{18}H_{15}N_4Cl,1\frac{1}{2}H_2O$, forms hard, granular crystals, which exhibit a brilliant metallic lustre; it becomes anhydrous at 120—130°, and is then hygroscopic. One litre of water dissolves 5·5 grams of the salt at 24°. The *free base* separates from water in green lamellæ having a well-marked metallic lustre. A litre of water dissolves 2·23 grams, and a litre of alcohol (90°) 9·09 grams of the base at 20°.

Measurements of the electrical conductivities of aqueous solutions of the two hydrochlorides show that for equal concentrations the azophenosafranine salt is a better conductor than its isomeride, and this divergence increases with greater dilution, the conductivity of the indophenosafranine salt remaining fairly constant, whilst that of its isomeride increases.

The absorption of light by aqueous solutions of the two salts is qualitatively the same, and ranges from the middle of the green to the beginning of the indigo, with a maximum where the green passes into the blue. Indophenosafranine hydrochloride shows a greater absorption than the isomeric salt except for light $\mu = 549$. T. A. H.

[A New Method of Formation of Diazo-compounds and a General Method for determining the Constitution of Azo-dyes.] OTTO SCHMIDT (*Ber.*, 1905, **38**, 4022—4023).—The author had overlooked in his recent paper (Abstr., 1905, i, 951) the earlier work (Meldola and Morgan, Trans., 1889, **55**, 608; Meldola and Hanes, *ibid.*, 1894, **65**, 841; Meldola and Southerden, Proc., 1894, **10**, 118) in this connection. W. A. D.

Examination of Proteid Preparations. PETER BERGELL (*Chem. Centr.*, 1905, ii, 1103—1104; from *Med. Klin.*, **1**, 1042—1045).—The examination of a proteid preparation is described for the case of gliadin, which is obtained from the best wheat meal by a purely mechanical method which depends mainly on a centrifugal process. In the dough thus prepared, 87·85 per cent. of the proteids, 90 of the fats, and 64·4 of the mineral substances of the original meal are present. After washing, drying, and grinding to an extremely fine powder, the air-dried substance contains 1·35 per cent. of nitrogen, 9·8 of water, and 6·2 of substances soluble in alcohol (lecithin), and yields 0·52 of ash. After completely extracting with alcohol, the residue contains 49·32 per cent. of carbon, 7·27 of hydrogen, 16·15 of nitrogen, and 0·701 of sulphur.

[With TH. DÖRPINGHAUS.]—When hydrolysed, the pure substance yields 1·2 per cent. of humin substances, 34·17 of glutamic acid, and rather less than 1 of tyrosine. About 5 per cent. of the nitrogen is present in the form of diamino-acids. The hydrolysis shows that two-thirds of the weight of the substance consists of monoamino-acids and that these acids contain 60 per cent. of the carbon of the gliadin. Alanine, leucine, pyrrolidine-2-carboxylic acid, phenylalanine, aspartic acid, and glycollic acid were also isolated. Gliadin is distinctly peptonised by the action of highly active gastric juice of dogs and is also directly attacked by pancreatin.

Clinical experiments on gliadin and its preparations are also described in the original paper. E. W. W.

Artificial Change of Albumin into Globulin. LEOPOLD MOLL (*Beitr. chem. Physiol. Path.*, 1905, **7**, 311—312. Compare Abstr., 1904, i, 356).—Further details in support of the author's previous contention that the naturally occurring pseudo-globulin of horse's blood is identical with that prepared artificially from the crystallised albumin of the same blood. W. D. H.

The Monoamino-acids of Crystallised Egg-albumin. EMIL ABDERHALDEN and FRITZ PREGL (*Zeit. physiol. Chem.*, 1905, **46**, 24—30).—The following products were separated out and estimated; the numbers given are the amounts obtained from 100 grams of ash-free, crystallised egg-albumin: alanine, 2·1; leucine, 6·1; pyrrolidine-2-carboxylic acid, 2·25; aspartic acid, 1·5; glutamic acid, 8·0; phenylalanine, 4·4; tyrosine, 1·1; and cystine, 0·2 grams. W. D. H.

Artificial Digestion Experiments. EDWARD GUDEMAN (*J. Amer. Chem. Soc.*, 1905, **27**, 1436—1442).—A series of experiments has been made with the object of ascertaining the influence of the following substances on the artificial digestion of egg-albumin with pepsin or pancreatin. Salicylic, benzoic, boric, and sulphurous acids, "saccharin," sugar, vinegar, ethyl and methyl alcohols, sodium chloride, formaldehyde, smoke, "condensed smoke," creosote, hydrochloric, sulphuric, phosphoric and nitric acids, sodium salicylate, benzoate, sulphite, borate and carbonate, and sodium hydrogen sulphite. The results are tabulated. In an acid medium, the only preservatives or condiments which retarded the digestion when present in a proportion of 1 : 400 or less were salicylic acid, formaldehyde, smoke, "condensed smoke," and creosote. Salicylic acid did not retard the digestion when present in the proportion of 1 : 1000. Acid substances, when added to a neutral solution of the albumin, accelerated the digestion, which then proceeded normally as in an acid medium. On the other hand, the addition of alkaline preservatives to a neutral medium caused abnormal results, the action of the ferment being retarded. In an alkaline medium, preservatives and condiments were found to retard the digestion to an extent depending on the degree of alkalinity.

A similar series of experiments was carried out with various coloured substances and dyes. The results showed that of the various colouring matters tested, only ultramarine, burnt sienna, chrome yellow, and ponceau 2R affected artificial digestion with pepsin when present in the proportion of 1 : 400 or less. The synthetical colouring matters were found to be less active than animal or mineral colours and not more active than vegetable colouring matters. Vegetable and synthetical colouring matters are directly digested by pepsin and pancreatin. E. G.

Fibrinoglobulin. W. HUISKAMP (*Zeit. physiol. Chem.*, 1905, **46**, 273—279. Compare Abstr., 1905, i, 499).—Polemical. The author maintains the correctness of his views on the fibrinoglobulin question in spite of the criticisms of Heubner (Abstr., 1905, i, 725).
W. D. H.

Decomposition of Casein by means of Ozone. CARL D. HARRIES (*Ber.*, 1905, **38**, 2990—2992).—The action of ozone on casein in $N/10$ sodium hydroxide solution leads to the formation of a colourless, slightly acid solution, which contains nitrous and nitric acids, has only a slight reducing action on Fehling's solution, and does not contain hydrogen peroxide; after some time, it acquires a characteristic odour of melted sugar. When boiled with phenylhydrazine hydrochloride and sodium acetate, the solution yields a yellow, flocculent *osazone*, which decomposes at about 200°, has acid properties, and reduces Fehling's solution like lactosazone, but is only sparingly soluble in water. The osazone contains practically the whole of the phosphorus from the casein.

The solution, after treatment with ozone, yields with lead acetate a white precipitate; from this there is obtained on treatment with hydrogen sulphide a white *substance* in a yield of at least 30 per cent. of the original casein, which melts and decomposes at 135°, is readily soluble in water, has an acid reaction, and yields the same osazone as is obtained directly from the ozonised solution; the white substance contains almost 2 per cent. of phosphorus, more than 40 per cent. of oxygen, and about 5—7 per cent. of nitrogen.

On removal of the lead from the filtrate from the lead acetate precipitate and evaporation in a vacuum, there is obtained a gelatinous *substance* which is readily soluble in water and gives the biuret reaction and yields a white precipitate with phosphotungstic acid. G. Y.

Cleavage Products of Proteoses. PHOEBUS A. LEVENE (*J. Biol. Chem., New York*, 1905, **1**, 45—58).—The experiments fail to corroborate Pick's statement that heteroalbumose in contradistinction to protoalbumose contains abundant glycine and leucine, but little or no tyrosine. The most striking difference noted is in the proportion of lysine, not of arginine, as Hart stated. W. D. H.

Protagon. EDWARD R. POSNER and WILLIAM J. GIES (*J. Biol. Chem., New York*, 1905, **1**, 59—112).—A complete and critical discussion of the protagon controversy. The present experiments confirm the statement that protagon is a mixture of substances, some of which contain phosphorus, whilst some do not. The substance phrenosin (Thudichum) is identical with that named pseudocerebrin by Gamgee,

and cerebrone by Thierfelder. It is always present in protagon. The name phrenosinic acid is suggested for Thudichum's neurostearic acid.
W. D. H.

Nature of Blood Pigments. M. Piettre and A. Vila (*Compt. rend.*, 1905, **141**, 734—736. Compare Cazeneuve and Breteau, Abstr., 1899, i, 840; ii, 440; Nencki and Sieber, Abstr., 1885, 69, 825; 1900, i, 709; 1901, i, 434).—Following Nencki's method (compare Abstr., 1900, i, 709), the authors have obtained crystalline acetylhæmi identical with the compound he described having the composition

$$C_{34}H_{33}O_4N_4ClFe;$$

if, however, the substance is prepared in a medium free from chlorides, the quantity of chlorine in the compound diminishes and the quantity of iron increases, whilst a specimen prepared from pure crystallised oxyhæmoglobin is free from chlorine and contains 9·20 per cent. of iron, Nencki's compound containing 5·44 per cent. of chlorine and 8·59 per cent. of iron. In view of these facts the authors are of opinion that the Teichmann-Nencki blood crystals do not consist of a definite chemical compound.
M. A. W.

Crystallised Hæmatin. M. Piettre and A. Vila (*Compt. rend.*, 1905, **141**, 1041—1044. Compare preceding abstract).—Crystallised hæmatin, obtained by extracting crystalline oxyhæmoglobin with methyl alcohol containing 3 per cent. of formic acid, forms black needles with a steel-blue reflex which resemble hæmin or acetylhæmin and deviate the plane of polarised light. The absorption spectrum in acid solution shows four characteristic absorption bands having their centres at $\lambda = 630$, 575, 534, and 494 respectively; in ammoniacal solution, the two latter bands persist, but in place of the two former there is a well-marked band with centre at $\lambda = 606$.

A substance of the nature of a higher fatty acid having C = 76·6 and H = 10·67 per cent. has been obtained from crystallised hæmatin, and the same compound has been prepared similarly from amorphous hæmatin, acetylhæmin, and hæmin.
M. A. W.

[Oxidation of Nucleic Acid.] Friedrich Kutscher (*Zeit. physiol. Chem.*, 1905, **46**, 305—306. Compare Abstr., 1905, i, 621, 725).—A reply to Burian. Polemical.
W. D. H.

Nucleic Acid of the Intestine. Katsuji Inouye and Y. Kotake (*Zeit. physiol. Chem.*, 1905, **46**, 201—205. Compare Abstr., 1904, i, 837).—The following seven substances were identified among the cleavage products of the nucleic acid from the intestine: lævulic acid, guanine, adenine, xanthine, hypoxanthine, thymine, cytosine.
W. D. H.

The Monoamino-acids of Keratin from Horse-hair. Emil Abderhalden and H. Gideon Wells (*Zeit. physiol. Chem.*, 1905, **46**, 31—39).—One hundred grams of ash-free, water-free, and melanin-free keratin, prepared from horse-hair, yielded, on hydrolysis, glycine, 4·7; alanine, 1·5; aminovaleric acid, 0·9; leucine, 7·1; pyrrolidine-2-carb-

oxylic acid, 3·4; aspartic acid, 0·3; glutamic acid, 3·7; tyrosine, 3·2 and serine, 0·6 grams.
W. D. H.

The Monoamino-acids of Keratin from Goose Feathers. Emil Abderhalden and E. R. Le Count (*Zeit. physiol. Chem.*, 1905, **46**, 40—46).—One hundred grams of ash-free and water-free keratin prepared from goose-feathers yielded, on hydrolysis, glycine, 2·6; alanine, 1·8; aminovaleric acid, 0·5; leucine, 8·0; pyrrolidine-2-carboxylic acid, 3·5; glutamic acid, 2·3; aspartic acid, 1·1; tyrosine, 3·6; and serine, 0·4 grams.
W. D. H.

Synthesis of a Substance allied to Adrenaline. Physiological Activity of Substances indirectly related to Adrenaline. Henry D. Dakin (*Proc. Roy. Soc.*, *B*, **76**, 491—497, 498—503).—A more detailed account of work already published (Proc., 1905, **21**, 154; Abstr., 1905, ii, 410).
G. S.

Epinephrine [Adrenaline] Hydrate. John J. Abel and Réne de U. Taveau (*J. Biol. Chem.*, *New York*, 1905, **1**, 1—32).—The empirical formula $C_{10}H_{13}O_3N.\frac{1}{2}H_2O$, which Abel originally assigned to epinephrine hydrate, is adhered to for reasons fully stated in the paper. There is, however, a lack of agreement in the nitrogen content of specimens prepared at different times and from different glands.
W. D. H.

The Co-enzyme of Zymase. Eduard Buchner and Wilhelm Antoni (*Zeit. physiol. Chem.*, 1905, **46**, 136—154).—Harden and Young (Abstr., 1905, ii, 109) state that boiled yeast juice contains a co-enzyme which increase the activity of the yeast zymase. The experiments now recorded show that the favouring action of the boiled juice is due to dilution of the mixture and the presence of phosphates in the boiled juice. Lecithin also has a slight favouring action.
W. D. H.

Casein as an Acid and its Distinction from Casein altered by Rennet (Paracasein). Action of Rennet. Ernst Laqueur (*Beitr. chem. Physiol. Path.*, 1905, **7**, 273—297).—A comparison of the properties of solutions of casein and paracasein (or, as they are usually called in English, caseinogen and casein respectively) is made, chiefly in relation to their acidity and electrical conductivity. Some modifications of the accepted theories of rennet action are suggested. The action of the ferment is believed to be in part synthetical.
W. D. H.

A Comparison between Organic and Inorganic Ferments. Peter Bergell (*Chem. Centr.*, 1905, ii, 1310—1311; from *Zeit. Klin. Med.*, **57**, 381—384).—Analogies are pointed out between enzymes and their activities and inorganic catalysing agents and their actions.
W. D. H.

Organic Chemistry.

Theory of the Grignard Reactions. RICHARD ABEGG (*Ber.*, 1905, **38**, 4112—4116. Compare Abstr., 1904, ii, 475).—It has been already suggested that alkyl groups are amphoteric in character; in compounds such as ethyl chloride they have electro-positive properties and, on hydrolysis, yield alcohols, whilst in metallic alkyl compounds such as zinc ethyl they have electro-negative properties and, on hydrolysis, yield hydrides (paraffins). The Grignard reactions permit of similar conclusions being drawn with reference to the electrochemical character of other organic radicles, and nine examples of different types are discussed from this point of view. Attention is called to the close analogy between the influence of electrical polarity in determining the direction of chemical change in electrolytes and in non-electrolytes, and to the fact that evidence of feeble ionisation has been obtained in the case of a few compounds generally regarded as non-electrolytes, for example, sugar, alcohol, ethyl malonate, and oxonium compounds. T. M. L.

Decomposition of Chloroform under the Influence of Light and Air. NICOLAAS SCHOORL and L. M. VAN DEN BERG (*Chem. Centr.*, 1905, ii, 1623; from *Pharm. Weekblad*, **42**, 877—888).—Quantitative experiments have shown that when chloroform is decomposed by the action of light in the presence of an excess of oxygen, carbon dioxide, water, and chlorine are formed, but that when insufficient oxygen is present, carbon oxychloride and hydrogen chloride are produced in molecular proportion. The latter conditions usually obtain in practice. E. W. W.

Readiness of Formation of Cyclic Compounds. PAVEL IW. PETRENKO-KRITSCHENKO and A. KONSCHIN (*Annalen*, 1905, **342**, 51—59).—After surveying the known data bearing on the formation of closed rings from open chains, the conclusion is drawn that the readiness, or better the velocity, of formation of cyclic compounds from open chains depends on two factors, the work necessary to bring the open chain into a cyclic position and the work required to actually close the ring.

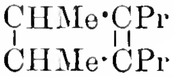
The velocities of the reaction between potassium hydroxide and various glycol monochlorohydrins and between dibromides and zinc dust are measured. The investigation of ethylene chlorohydrin, trimethylene chlorohydrin, γ-pentylene chlorohydrin, and δ-hexylene chlorohydrin shows that there is a marked difference in the velocity of the reaction between the α-compounds and the β-compounds, whilst the remainder of the substances investigated behave in much the same way. The velocity of decomposition of γ-pentylene chlorohydrin is slightly greater than that of the others.

The velocity of the reaction of the dibromides with zinc dust is expressed as a percentage of the material which has been decomposed in one hour: ethylene dibromide, 19·87; propylene dibromide, 20·87; trimethylene bromide, 2·02; γ-pentylene dibromide, 1·80; pentamethylene dibromide, 1·25; δ-hexylene dibromide, 1·92.

The opinion is expressed that in the case of the compounds investigated, unlike the acid compounds, the "tension" of the ring which is formed does not play an important part in determining the velocity of the reaction. K. J. P. O.

Action of Dilute Sulphuric Acid on the Pinacone formed from Ethyl Propyl Ketone. Felix Goldberger and Rudolf Tandler (*Monatsh.*, 1905, **26**, 1473—1485. Compare Zumpfe, Abstr., 1904, i, 291; Lieben, Abstr., 1905, i, 167; Kohn, *ibid.*).—The pinacone obtained in a yield of 28 per cent. of the theoretical, by reduction of ethyl propyl ketone with sodium and water, or in poorer yield by electrolytic reduction in dilute sulphuric acid solution, with a current density of 8 amperes per square decimetre, boils at 125—126° under 11 mm., or at 254—255° under the atmospheric pressure (Oechsner de Coninck, Abstr., 1876, i, 694). When heated with 20—30 per cent. sulphuric acid in a sealed tube at 170—180° for six hours, it yields an unsaturated hydrocarbon and an oxide.

The *hydrocarbon*,



$\begin{matrix}\mathrm{CHMe{\cdot}CPr}\\ |\qquad\ \|\\ \mathrm{CHMe{\cdot}CPr}\end{matrix}$

(?), is a colourless oil, which has an odour of camphor, boils at 75—76° under 11 mm. or at 194—195° under the atmospheric pressure, forms a dark, resinous *additive* compound with 1 mol. of bromine in carbon disulphide solution, and when oxidised with nitric acid of sp. gr. 1·5 under cooling, or with alkaline permanganate solution at 60°, yields carbon dioxide and an *acid*; this is volatile with steam and forms a *silver* salt, $C_4H_7O_2Ag$.

The *oxide*, $C_{12}H_{24}O$, is a slightly yellow liquid having a burning odour, which boils at 105—106° under 11 mm. or at 225° under atmospheric pressure, and is easily soluble in ether, alcohol, or chloroform. It does not form an oxime, a sodium hydrogen sulphite additive compound, or an acetyl derivative when boiled with acetyl chloride; it remains unchanged when boiled with sodium in an atmosphere of hydrogen, or when heated with zinc ethyl in a sealed tube at 150° for three hours, or with water under pressure at 180—200°. It must be therefore an αγ- or an αδ-oxide. It is not reduced by alcohol and sodium, and does not interact with magnesium ethyl iodide; when oxidised with alkaline permanganate solution, it yields a mixture of acids, which forms silver butyrate and a *silver* salt, $C_7H_{13}O_2Ag$, crystallising in white needles. G. Y.

Synthesis in the *s*-Heptane-αδη-triol Series. Jules L. Hamonet (*Compt. rend.*, 1905, **141**, 1244—1245).—*αη-Dimethoxyheptane-δ-ol*, $OH{\cdot}CH(CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OMe)_2$, prepared by the action of ethyl formate on the magnesium derivative of γ-iodo-α-methoxypropane (compare Abstr., 1904, i, 467), is a colourless, slightly odorous liquid with a very bitter taste, which boils at 141—142° under 21 mm. or at 246—248° under the ordinary pressure, has a sp. gr. 0·969 at 18°, and does not crystallise when cooled in a mixture of solid carbon dioxide and acetone. *δ-Chloro-αη-dimethoxyheptane*, $C_7H_{13}Cl(OMe)_2$, prepared by the action of phosphorus trichloride on the alcohol, is a colourless, mobile liquid with an agreeable odour, boiling at 120° under 16 mm. pressure and having a sp. gr. 1·001 at 18°. αδη-*Tribromoheptane*, $C_7H_{13}Br_3$, prepared by heating the alcohol with acetic acid and hydrobromic acid in sealed tubes at 100°, is a viscous liquid, solidifying in a mixture of solid carbonic acid and acetone, boiling at 184—185° under 19 mm. pressure, and having a sp. gr. 1·775 at 18°. αδη-*Tri-iodoheptane*, $C_7H_{13}I_3$, obtained by the action of hydrogen iodide in the cold on the alcohol, is a slightly coloured, viscous liquid, having a sp. gr. 2·343 at 18°, which cannot be distilled without decomposition.

M. A. W.

Halogenated Aliphatic Acids. Wilhelm Lossen (*Annalen*, 1905, **342**, 112—155, 157—190).—It has been shown (Abstr., 1893, i, 142) that both dibromosuccinic acid and *iso*dibromosuccinic acid, the latter more easily, are converted by the action of alkali hydroxides into acetylenedicarboxylic acid, a fact which is not in agreement with Wislicenus's views as to the stereoisomerism of the two dibromosuccinic acids. A new series of experiments has been undertaken with the object of throwing light on this difference.

[With Robert Eichloff.]—Chloro- and bromo-acetic acids were converted by aqueous or alkaline solutions into glycollic acid at different temperatures, and the velocity of the hydrolysis measured. The change is accelerated by raising the temperature, and the velocity is greater in solutions containing molecular proportions of the acid and the base than in aqueous solutions. Increase, however, in the concentration of the alkali greatly hastens the velocity of the reaction. In dilute solution, the free acid decomposes far more rapidly than in concentrated solution, but in presence of alkali the reverse is the case. Bromoacetic acid under all conditions decomposes more rapidly than chloroacetic acid.

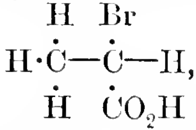
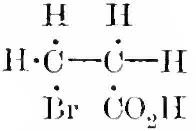
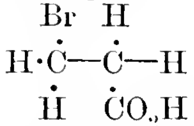
Chloroacetic acid yields not only glycollic acid but also diglycollic acid when boiled with bases, the particular reaction depending on the nature and quality of the base. Bromoacetic acid was investigated. Normal sodium hydroxide yields only glycollic acid, concentrated sodium hydroxide (1 molecule of base to 1 of acid) gives also glycollic acid, but 2 molecules of the concentrated base yield diglycollic acid and glycollic acid in the proportion of 1 : 2·8, and 3 molecules of the base gave the two acids in the proportion of 1 : 1·7. It is noteworthy that potassium hydroxide in place of sodium hydroxide increases the proportion of diglycollic acid. Barium hydroxide in neutral solution converts the bromoacetic acid into glycollic acid, but if two equivalents of the base are present for every equivalent of acid, 76 per cent. of diglycollic acid is formed.

When boiled with water, both trichloro- and tribromo-acetic acids are decomposed into chloroform and carbon dioxide. If the decomposition is effected by sodium hydroxide in the proportion of 6 molecules of base to 1 of acid, the reaction is represented by the equation:

$$CCl_3\cdot CO_2H + 6NaOH = 3NaCl + HCO_2Na + Na_2CO_3 + 3H_2O.$$

If less sodium hydroxide is used, the two reactions occur together.

[With Eugen Kowski.]—α-Bromopropionic acid yields both lactic and acrylic acids, behaving in the manner above stated. Barium hydroxide has a somewhat different action from sodium hydroxide, giving other proportions of the two acids.

β-Bromopropionic acid yields hydracrylic and acrylic acids, the latter forming a larger proportion of the product than in the case of α-bromopropionic acid. The decomposition also takes place more rapidly. This fact is not in agreement with Wislicenus' theory as to the mechanism of the elimination of hydrogen haloids from organic compounds. α-Bromopropionic acid,  $\mathrm{H{\cdot}\overset{H}{\underset{H}{\dot{C}}}{-}\overset{Br}{\underset{CO_2H}{\dot{C}}}{-}H}$, should yield acrylic acid more easily than β-bromopropionic acid, which has either the configuration  $\mathrm{H{\cdot}\overset{H}{\underset{Br}{\dot{C}}}{-}\overset{H}{\underset{CO_2H}{\dot{C}}}{-}H}$ or  $\mathrm{H{\cdot}\overset{Br}{\underset{H}{\dot{C}}}{-}\overset{H}{\underset{CO_2H}{\dot{C}}}{-}H}$; the first configuration alone would yield acrylic acid, whilst the second would give ethylene, carbon dioxide, and sodium bromide.

αα-Dibromopropionic acid gives pyruvic and α-bromoacrylic acids and the so-called acryl-colloid; the velocity of the decomposition is affected by bases in the same way as with the foregoing substances. The proportion of α-bromoacrylic acid decreases with increasing dilution; it crystallises in readily volatile plates melting at 68°, and is decomposed by exposure to the air, or by treatment with sodium hydroxide, into acetylene. The acryl-colloid is formed only in acid solution; it consists of a jelly which, when dry, has the composition $C_{3n}H_{4n}O_{3n}$, and is completely insoluble in water, but soluble in alkali hydroxides. It is probably a polymeride of pyruvic acid, since ether extracts from the alkaline solution after acidification a syrup which combines with phenylhydrazine yielding the phenylhydrazide of pyruvic acid.

αβ-Dibromopropionic acid decomposes more rapidly than the αα-isomeride, yielding glyceric acid and α-bromohydracrylic acid, together with small quantities of pyruvic acid or, in acid solution, of acryl-colloid. According to Wislicenus' theory, the αα- should decompose more rapidly than the αβ-acid, since it can exist in only one configuration, namely, that which would yield bromohydracrylic acid.

[With HUGO SMELKUS.]—The main product of the decomposition of α-bromobutyric acid is hydroxybutyric acid, but both crotonic acid and *s-diethyldiglycollic* (*butodiglycollic*) *acid*,

$$CO_2H{\cdot}CHEt{\cdot}O{\cdot}CHEt{\cdot}CO_2H,$$

are also formed. The latter is best prepared by dropping bromobutyric acid on to solid sodium hydroxide, mixing, and, after acidifying with dilute sulphuric acid, separating the oily layer, which consists mainly of crotonic acid, and then extracting the new acid with ether and purifying in the form of the barium salt. The acid crystallises at a low temperature and melts at 26°; it boils at 117° under 11 mm. pressure. The normal *potassium* salt, $C_8H_{12}O_5K_2$, crystallises in hygroscopic needles, whilst the *potassium hydrogen* salt, $C_8H_{13}O_5K,\frac{1}{2}H_2O$, forms rectangular plates. The normal *sodium* salt, $C_8H_{12}O_5Na_2$, crystallises in leaflets or needles, and the acid *salt*,

$$2C_8H_{13}O_5Na,C_8H_{14}O_5,H_2O,$$

forms needles. The *ammonium* salt crystallises in anhydrous needles, the *calcium* salt, $C_8H_{12}O_5Ca,H_2O$, forms microscopic prisms, the *barium* salt, $C_8H_{12}O_5Ba,\frac{1}{2}H_2O$, prisms, and the *copper* salt, $C_8H_{12}O_5Cu,H_2O$, pale blue needles; when anhydrous, the latter is deep azure blue. The *silver* salt, $C_8H_{12}O_5Ag_2$, crystallises in quadratic prisms, and the *lead* salt, $C_8H_{12}O_5Pb$, is amorphous.

s-*Diethyldiglycollimide*, $C_8H_{12}O_3{:}NH$, is prepared by dry distillation of the ammonium salt, and is a fusible solid distilling at 200—215°. *s*-Diethyldiglycollic acid can be distilled under diminished pressure, but at the ordinary pressure decomposes into carbon monoxide and propaldehyde and an acid which appears to be metameric with *α*-hydroxybutyric acid. When reduced with 50 per cent. hydriodic acid, *s*-diethyldiglycollic acid yields butyric acid and hydroxybutyric acid.

[With Oscar Gerlach.]—When *α*-bromo*iso*butyric acid is decomposed by treatment with water at the ordinary temperature, a process which requires eighteen months, hydroxy*iso*butyric acid is alone produced, whereas by boiling with water 8 per cent. of methylacrylic acid is also formed; 14·8 per cent. of methylacrylic acid is formed when 1 mol. of *N*NaOH is used at a temperature of 80°, and 75 per cent. when 4 mols. of 25 per cent. sodium hydroxide are employed.

β-Bromo*iso*butyric acid yields only methylacrylic acid under all conditions. Wislicenus' theory indicates that the *α*-bromo-acid would yield methylacrylic acid rather than the *β*-bromo-acid.

Zinc methylacrylate, $(C_4H_5O_2)_2Zn$, crystallises in prisms and readily polymerises when heated. The *cadmium* salt forms small aggregates, the *strontium* salt needles, and the *lead* salt prisms or plates which polymerise on heating; the *copper* salt is a pale blue, insoluble precipitate.

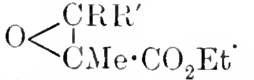
[With Fritz Morschöck and Carl Dorno.]—Bromomethylacrylic acid is formed when *citra*dibromomethylsuccinic acid is boiled with three parts of water for four hours. Both bromo- and *iso*bromo methacrylic acids are formed when a neutral solution of *meso*dibromomethylsuccinic acid is warmed at 60°, care being taken that the solution remains neutral. The bromo-acid separates first, whilst the *iso*bromo-acid can be extracted with ether. *iso*Bromomethylacrylic acid crystallises in leaflets melting at 68°. Both acids decompose on heating into hydrogen bromide, carbon dioxide, and allene. When boiled for a short time, the *iso*bromomethylacrylic acid is converted into bromomethylacrylic acid, but on prolonged boiling with aqueous sodium hydroxide both acids are decomposed, the *iso*-acid more slowly, into allylene. Heating of the calcium salts produces allene and allylene, the *iso*-acid being first transformed into bromomethylacrylic acid. This change is also effected by exposure of the chloroform solution, to which a trace of bromine has been added, to sunlight. The silver salts of both acids are decomposed on boiling with water, that of bromomethylacrylic acid yielding silver bromide, silver, carbon dioxide, and propaldehyde. The silver salt of the *iso*-acid changes more rapidly than the other according to the equation $C_4H_4O_2BrAg + H_2O = C_3H_6O + CO_2 + AgBr$. Permanganate oxidises both acids to acetic acid; a similar behaviour of the two acids is also observed when reduced or electrolysed.

[With Carl Dorno.]—Allene yields a *compound* with aqueous mercuric chloride, which has the composition $C_6H_8O_3Cl_6Hg_6$ and seems to be identical with the substance obtained from allylene by Kutscheroff (*Ber.*, 1884, **17**, 13). In order to distinguish the two gases, dependence is especially to be placed on the fact that allylene precipitates ammoniacal silver and cuprous solutions, whilst allene does not. With alkaline mercury solutions, allylene gives a precipitate, $(C_3H_3)_2Hg$; allene does not. The tetrabromide of allylene is liquid and that of allene a solid melting at 0°. K. J. P. O.

Action of Cyanoacetic Acid on Crotonaldehyde. Hugo Haerdtl (*Monatsh.*, 1905, **26**, 1391—1402. Compare Braun, Abstr., 1896, i, 594; Doebner, Abstr., 1900, i, 536).—α-Cyanosorbic acid, $CHMe{:}CH{\cdot}CH{:}C(CN){\cdot}CO_2H$, is formed by heating a molecular mixture of crotonaldehyde and cyanoacetic acid in an atmosphere of carbon dioxide, in a reflux apparatus, in a boiling water-bath for six hours. It crystallises from water in stout, yellow needles, 6—8 mm. long, softens and loses carbon dioxide at 150°, or melts and decomposes at 163° when quickly heated. The *barium* salt,

$$(C_7H_6O_2N)_2Ba,\tfrac{1}{2}H_2O,$$

crystallises in nodular aggregates. With bromine in chloroform solution, the cyano-acid forms the *additive* compound, $C_7H_7O_2NBr_2$, which separates as a fine, white, crystalline powder and melts at 154—156°. When heated in small quantities at 150—160° until the evolution of carbon dioxide ceases, the cyano-acid forms *sorbonitrile*, $CHMe{:}CH{\cdot}CH{:}CH{\cdot}CN$, which, when freshly distilled, is a clear, mobile liquid; it boils at 50—60° under 12 mm. pressure and gradually decomposes in a closed vessel with formation of a brown resin. When boiled with 10—12 per cent. aqueous potassium hydroxide in a reflux apparatus, the cyano-acid yields a brown, amorphous *substance*, $C_6H_8O_2$(?), which is soluble in pyridine or glacial acetic acid, but is insoluble in aqueous sodium carbonate, and when boiled with aqueous baryta forms a *barium* salt, $(C_4H_5O_2)_2Ba$, whilst no definite product of hydrolysis could be obtained by heating the cyano-acid with alcoholic potassium hydroxide, dilute hydrochloric acid, or 40 per cent. sulphuric acid. G. Y.

General Method of Synthesising αβ-Trisubstituted Glycidic Esters and Ketones. Georges Darzens (*Compt. rend.*, 1905, **141**, 766—768. Compare Abstr., 1905, i, 116).—Ethyl α-chloropropionate readily condenses with ketones in the presence of sodium ethoxide to form the ethyl esters of the αβ-trisubstituted glycidic acids of the type  $\mathrm{O}\Big<\begin{matrix}\mathrm{CRR'}\\ |\\ \mathrm{CMe\cdot CO_2Et}\end{matrix}$. These are colourless liquids with a faint odour, yielding on hydrolysis the corresponding acids, which are unstable and readily break down into carbon dioxide and the corresponding ketone, the latter being formed probably from an intermediate oxide by the migration of a hydrogen atom (compare Fourneau and Tiffeneau, this vol., i, 20), according to the equations:

$$\mathrm{O}\Big<\begin{matrix}\mathrm{CRR'}\\ |\\ \mathrm{CMe\cdot CO_2H}\end{matrix} = CO_2 + \mathrm{O}\Big<\begin{matrix}\mathrm{CRR'}\\ |\\ \mathrm{CHMe}\end{matrix}; \quad \mathrm{O}\Big<\begin{matrix}\mathrm{CRR'}\\ |\\ \mathrm{CHMe}\end{matrix} = \mathrm{CHRR'{\cdot}COMe}.$$

In the following table are given the boiling points of the new ethyl trisubstituted glycidates and of the ketones prepared from them, together with the melting points of the semicarbazides of the latter.

Ketone.	Boiling point of corresponding ethyl glycidate.	Pressure.	Boiling point of ketone.	Pressure.	Melting point of semi-carbazide.
Acetone....................	80—82°	under 20 mm.	—		—
Methyl ethyl ketone ...	90—93	,, 22 ,,	—		—
Methyl *n*-propyl ketone	100—102	,, 16 ,,	—		—
Methyl *n*-hexyl ,,	152	,, 28 ,,	100—103°	under 26 mm.	86—87°
Methyl *n*-heptyl ,,	148—150	,, 16 ,,	101—103	,, 15 ,,	168—169
Methyl *n*-nonyl ,,	174—175	,, 15 ,,	132—135	,, 15 ,,	78—79
Acetophenone	151—154	,, 22 ,,	102—104	,, 20 ,,	172—173
p-Tolyl methyl ketone..	160—162	,, 19 ,,	116—118	,, 22 ,,	184—185

M. A. W.

Preparation of Pure Ethyl Alkylmalonates. Arthur Michael (*J. pr. Chem.*, 1905, [ii], 72, 537—554. Compare Abstr., 1905, i, 564, 855).—On adding ethyl malonate to the equivalent amount of 50 per cent. aqueous potassium hydroxide, cooled to – 10°, the mixture solidifies owing to the formation of ethyl potassiomalonate, which rapidly decomposes to ethyl potassium malonate and alcohol. This change takes place immediately when ethyl malonate is shaken with 1 per cent. aqueous potassium hydroxide.

The partial hydrolysis of ethyl ethylmalonate takes place in less than one minute with 1 per cent., in three minutes with 4 per cent., in thirty minutes with 12 per cent., and only to the extent of 20 per cent. in thirty minutes, with 25 per cent. aqueous potassium hydroxide. When shaken with 25 per cent. aqueous potassium hydroxide, a mixture of ethyl ethylmalonate and ethyl malonate develops heat, and if extracted with ether after one minute yields 86 per cent. of the ethyl ethylmalonate in a state of purity.

Ethyl diethylmalonate undergoes only slight hydrolysis when heated with 50 per cent. aqueous potassium hydroxide.

The propylmalonates resemble the ethylmalonates in their stability towards alkali hydroxides, whilst the methylmalonates undergo hydrolysis more easily, ethyl dimethylmalonate being hydrolysed rapidly with 50 per cent. aqueous potassium hydroxide.

These differences in behaviour are utilised in the detection of ethyl malonate and ethylmalonate, the presence of 1 and 2 per cent. of which, respectively, causes the formation of a white precipitate when ethyl diethylmalonate is shaken with 50 per cent. aqueous potassium hydroxide, and of ethyl diethylmalonate, small percentages of which appear as drops of oil, when ethyl ethylmalonate or malonate is shaken with dilute potassium hydroxide.

Application of these tests to the ethyl ethylmalonates obtained by the methods used by previous authors shows that these contain varying quantities of ethyl diethylmalonate which cannot be removed by fractional distillation or by Schey's method of purification (*Rec. Trav. chim.*, 1897, 16, 357).

To prepare pure ethyl ethylmalonate, the crude product is shaken with 25 per cent. aqueous potassium hydroxide and the resulting oil boiled with an excess of the same reagent in a reflux apparatus. After extracting the ethyl diethylmalonate with ether, the solution is again boiled with a further quantity of potassium hydroxide, neutralised with hydrochloric acid, and treated with calcium chloride. The calcium salt obtained in this manner yields pure ethyl ethylmalonate, which boils at 92° under 10 mm., or at 211° (corr.) under 748 mm. pressure, and has a sp. gr. 1·004 at 20°.

Ethyl diethylmalonate is purified by boiling with 50 per cent. aqueous potassium hydroxide; it boils at 228·5—229·5° (corr.).

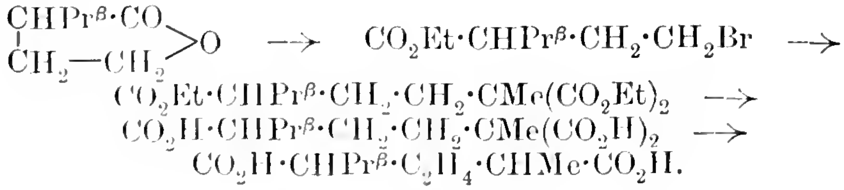
Ethyl methylmalonate, prepared by the action of methyl iodide on ethyl sodiomalonate and purified in the same manner as ethyl ethylmalonate, boils at 198·5—199° (corr.) under 765 mm. pressure. Ethyl dimethylmalonate, purified by shaking with a small quantity of 25 per cent. aqueous potassium hydroxide, boils at 196—196·5° (corr.) under 753 mm. pressure.

Ethyl propylmalonate boils at 225·5—226° (corr.) under 771 mm. pressure, and has a sp. gr. 0·9897 at 25°/25°. Ethyl dipropylmalonate boils at 248—249° (corr.).

Ethyl methylmalonate and ethylmalonate are obtained in yields of 90 and 70 per cent. of the ethyl malonate used when mixtures of ethyl malonate and methyl and ethyl iodide respectively are shaken with finely-divided potassium hydroxide. Ethyl dimethylmalonate is formed in the same manner from ethyl methylmalonate.

When shaken with ethyl iodide and powdered potassium hydroxide, ethyl acetoacetate forms ethyl ethylacetoacetate in a yield of 70—80 per cent. of its own weight, but in small yields in presence of water. The action of ethyl iodide and potassium hydroxide on ethyl ethylacetoacetate takes place only slowly and incompletely. G. Y.

Synthesis of Dihydrocamphoric Acid. Gustave Blanc (*Compt. rend.*, 1905, **141**, 1030—1032).—The author has confirmed the constitution ascribed by Martine (Abstr., 1902, i, 629) to dihydrocamphoric acid, namely, α-methyl-δ-*iso*propyladipic acid (compare Perkin and Crossley, Trans., 1898, **73**, 23), by its synthesis from *iso*propylsuccinic anhydride (Abstr., 1904, i, 369, 647; 1905, i, 631). *iso*Propylsuccinic anhydride on reduction yields a mixture of α- and β-*iso*propylbutyrolactones, from which, on treatment with phosphorus pentabromide and subsequently with alcohol, a mixture of ethyl γ-bromo-α- and -β-*iso*propylbutyrates is obtained, of which the α-isomeride condenses with ethyl sodiomethylmalonate to form a tricarboxylic ester. The corresponding free acid melts at 158°, losing carbon dioxide and forming α-methyl-δ-*iso*propyladipic acid, according to the equations:



$$\begin{matrix}\mathrm{CHPr^{\beta}\cdot CO}\\ |\\ \mathrm{CH_2—CH_2}\end{matrix}\!\!>\!\mathrm{O} \longrightarrow \mathrm{CO_2Et\cdot CHPr^{\beta}\cdot CH_2\cdot CH_2Br} \longrightarrow$$

$$\mathrm{CO_2Et\cdot CHPr^{\beta}\cdot CH_2\cdot CH_2\cdot CMe(CO_2Et)_2} \longrightarrow$$

$$\mathrm{CO_2H\cdot CHPr^{\beta}\cdot CH_2\cdot CH_2\cdot CMe(CO_2H)_2} \longrightarrow$$

$$\mathrm{CO_2H\cdot CHPr^{\beta}\cdot C_2H_4\cdot CHMe\cdot CO_2H.}$$

α-Methyl-δ-*iso*propyladipic acid has all the properties of dihydrocamphoric acid except that it is racemic; dihydrocamphoric acid, contrary to the statement of Perkin and Crossley, is optically active, having $[\alpha]_D$ 8°30′ according to measurements made by Martine at the author's request. α-*iso*Propyladipic acid melting at 63° is obtained when ethyl sodiomalonate is substituted for ethyl sodiomethylmalonate in the above series of reactions. M. A. W.

Iron Citrates. GIUSEPPE SIBONI (*Chem. Centr.*, 1905, ii, 1623—1624; from *Boll. Chim. Farm.*, **44**, 625—637).—Ferrous citrate, prepared by boiling a solution of citric acid with iron turnings for several days and concentrating in a vacuum, is sparingly soluble in water, but does not crystallise readily owing to the formation of the more soluble ferric citrate. If oxidation is prevented, the citrate separates out even in the presence of free citric acid (compare Martinotti and Cornelio, Abstr., 1901, i, 667). Ferrous citrate is very readily soluble in ammonia, forming ferrous ammonium citrate (*loc. cit.*), which decomposes at 120° and is readily oxidised in solution, but is more stable in the presence of citric acid or an excess of acid ferrous citrate. Sodium ferrous citrate, prepared by neutralising crystalline ferrous citrate with sodium hydroxide, is more suitable for therapeutic application (compare Baroni, *Giorn. Farm. Chim.*, **53**, 145).

Normal ferric citrate, $C_6H_5O_7Fe,3H_2O$, is obtained by digesting freshly precipitated ferric hydroxide with citric acid for twenty-four hours at 60—65°, filtering, and evaporating the filtrate at 50—60°; an anhydrous salt separates from the aqueous solution in the form of a red powder on the addition of ether. Ferric citrate has an acid reaction, and when treated with ammonia forms ammino- and ammonium salts. The *monoammino*-salt, $2C_6H_5O_7Fe,NH_3$, forms a slightly deliquescent, red powder, which has an acid reaction and is not suitable for subcutaneous injection. The *diammino*-salt,

$$2C_6H_5O_7Fe,2NH_3,$$

prepared by the action of ammonia on an aqueous solution of the preceding salt or by the oxidation of ferrous ammonium citrate, is brown and more deliquescent than the monoammino-salt. The *triammino*-salt, $2C_6H_5O_7Fe,3NH_3$, obtained by saturating a solution of ferric citrate with ammonia, is neutral and better adapted for subcutaneous injection. *Ferric ammonium citrate*, $H_2(NH_4)Fe_2(C_6H_5O_7)_3$, prepared by adding a solution of ammonia to a solution of ferric citrate, forms thin, yellowish-brown scales, is very deliquescent, and has a strong acid reaction. *Ferric diammonium citrate*, $H(NH_4)_2Fe_2(C_6H_5O_7)_3$, also obtained by the action of ammonia on a solution of ferric citrate, forms yellowish-green scales and is very deliquescent. *Ferric triammonium citrate*, $(NH_4)_3Fe_2(C_6H_5O_7)_3$, also separates in bright green scales and has an acid reaction. The *tetra-ammonium* salt,

$$(NH_4)_3Fe_2(C_6H_5O_7)_3,NH_3,$$

prepared by neutralising a solution of ferric citrate with ammonia and evaporating at a low temperature, crystallises in scales. This salt is contained in the preparation described in the German Pharmacopœia; the preparations of the Russian and Norwegian Pharmacopœias should contain 9·21 and 17·33 per cent. of iron respectively. E. W. W.

Laboratory Notes. [Di*iso*butyl Ketone. *iso*Nitrosobenzylacetone. *iso*Butyryl- and *iso*Valeryl-phenylhydrazines. Erucic Acid.] GIACOMO PONZIO (*Gazzetta*, 1905, **35**, ii, 394—398).—Di*iso*butyl ketone (valerone), $CO(CH_2 \cdot CHMe_2)_2$, prepared by the action of zinc *iso*butyl on *iso*valeryl chloride, boils at 164—166° under 741 mm. pressure and gives a *semicarbazone*, $C_{10}H_{21}ON_3$, crystallising from light petroleum in white plates melting at 115° (compare Schmidt, *Ber.*, 1872, **5**, 600; Williams, Trans., 1879, **35**, 130).

*iso*Nitrosobenzylacetone can be obtained readily and in good yield by adding *iso*amyl nitrite and benzylacetone to alcoholic sodium ethoxide and subsequently washing the alkaline solution with ether and saturating it with carbon dioxide. It crystallises from light petroleum in long, shining needles melting at 80—81° (compare Ceresole, Abstr., 1883, 41).

With phenylhydrazine, *iso*butyryldinitroethane yields *iso*butyrylphenylhydrazine, whilst *iso*valeryldinitroethane gives *iso*valerylphenylhydrazine, *aa*-dinitroethane being formed in both cases.

On passing dry hydrogen bromide into a cold acetic acid solution of erucic acid, the latter is converted partly into the isomeric planosymmetric brassidic acid and partly into *bromobehenic acid*, $C_{22}H_{43}O_2Br$, which crystallises from alcohol in white prisms melting at 39—40°.

T. H. P.

Digitoxose. HEINRICH KILIANI (*Ber.*, 1905, **38**, 4040—4043. Compare Abstr., 1899, i, 932).—Digitoxose is considered now to have the constitution $OH \cdot CHMe \cdot CH(OH) \cdot CH(OH) \cdot CH_2 \cdot CHO$. It is an aldehyde, as, on oxidation with bromine in aqueous solution and removal of the hydrogen bromide which is formed by means of silver oxide, it yields a solution containing the *lactone* of digitoxonic acid; this, when boiled with calcium carbonate, forms *calcium digitoxonate*, $(C_6H_{11}O_5)_2Ca$, which is precipitated as a glutinous mass.

As digitoxosecarboxylic acid also forms a lactone, two of the hydroxyl groups of digitoxose must be in the β- and γ-positions, whilst the δ-position of the third hydroxyl is shown by the conversion of calcium digitoxonate into *aβ-dihydroxyglutaric acid* when it is oxidised with concentrated nitric acid under cooling with ice, and finally at 35—37°. The acid is isolated in the form of its *calcium* salt, $C_5H_6O_6Ca$, which is precipitated from its aqueous solution by means of alcohol, and on liberation from this, as its *lactone*, $C_5H_6O_5$. This is obtained as an oil, which, after some time, solidifies when stirred; it commences to soften at about 115°, melts at 120°, and differs from the previously known dihydroxyglutaric acids in that after cooling and resolidification it melts sharply at 120° (compare Kiliani and Herold, Abstr., 1905, i, 739; Kiliani and Loeffler, *ibid.*, 858); it is slightly dextrorotatory in 7·8 per cent. solution in a 2 dcm. tube.

G. Y.

Mineral Compounds which may possess the Rôle, like Diastase, of Liquefying Malt. JULES WOLFF (*Compt. rend.*, 1905, **141**, 1046—1048).—Starch (25 grams) was treated with 50 c.c. of a solution containing 0·1 per cent. of potassium permanganate and

10—15 per cent. of sulphuric acid (or 6—7 per cent. of hydrochloric acid) for $1\frac{1}{2}$ to 2 hours, washed with distilled water, and dried at 30°. The starch underwent no appreciable change in appearance or weight, and when treated with malt or acids yielded the same products as ordinary starch. When, however, a small amount of a basic substance (ammonia, alkaline oxides, &c.) is present and the temperature is raised to 70°, it liquefies immediately. Acids, neutral salts, and acid phosphates have no action.

When the starch, treated as described, is mixed with distilled water, the liquid is slightly acid (to phenolphthalein). The liquefaction does not, however, occur exactly at the point when the acid is just neutralised, but may take place both in slightly acid and in slightly alkaline conditions.

The change produced in the starch is not due to the removal of mineral salts. N. H. J. M.

Liquefying and Saccharifying Actions on Starch. Paul Petit (*Compt. rend.*, 1905, **141**, 1247—1249. Compare preceding abstract).—Infusions of malt behave like guaiacol towards ferrous, ferric, manganous, and manganic compounds. Ferric and manganic compounds of malt infusion are reduced by hydrogen. A known volume of sodium hydroxide solution is added to the infusion containing the aluminium compound in an atmosphere of hydrogen. The soda is then exactly neutralised with acetic acid and tincture of guaiacol added. No coloration is produced ; addition of a drop of hydrogen peroxide at once produces a strong blue colour.

A solution of commercial albumin (0·25 per cent.) was shaken with a mixture of equal parts of ferrous, ferric, and manganous oxides and filtered. The solution, which after a time became turbid, was again filtered. The clear liquid shows the same reaction with tincture of guaiacol as malt infusion, and it also liquefies starch, the action being accelerated by addition of asparagine. In presence of asparagine, there is also a slight saccharification. N. H. J. M.

Starch, Glycogen, and Cellulose. Zdenko H. Skraup [and, in part, E. Geinsperger, E. von Knaffl-Lenz, Franz Menter, and H. Sirk] (*Monatsh.*, 1905, **26**, 1415—1472).—Soluble starch was suspended in eight times its weight of acetic anhydride saturated with hydrogen chloride at $-20°$; after fourteen days at the laboratory temperature, the chief product was chlorononadeca-acetylerythrodextrin ; after two months, an amorphous substance, having the composition of acetylchloromaltose ; and after four months, tetra-acetylchlorodextrose.

Chlorononadeca-acetylerythrodextrin, $(C_6H_7O_5)_6ClAc_{19}$, is soluble in benzene, but insoluble in light petroleum, has $[\alpha]_D$ $+186·20°$, and when treated with silver acetate in glacial acetic acid solution yields the icosa-acetyl derivative, $(C_6H_7O_5)_5(C_6H_7O_6)Ac_{20}$, which sinters at 110° and has $[\alpha]_D$ $+145·3°$. When hydrolysed by means of $2N$ alcoholic potassium hydroxide, under cooling with snow, it yields erythrodextrin, having $[\alpha]_D$ $+160·8°$. The product obtained on shaking soluble starch with acetic anhydride, saturated with hydrogen chloride at 0°, for seven hours in a sealed tube at 40° is a mixture of acetylchloro-derivatives of the starch and its decomposition products. When purified by precipitation from its benzene solution by light petroleum and by ether, the *acetylchloro*-derivative of soluble starch contains 0·268 per cent. of chlorine, from which its molecular weight is calculated as 13230. It sinters at 170°, becomes brown at 240—250°, decomposes with evolution of a gas at 270°, does not give a coloration with iodine, and when hydrolysed with $2N$ alcoholic potassium hydroxide yields soluble starch. The minimum formula for soluble starch must be, therefore, $(C_6H_{10}O_5)_{46-50}$. When heated on the water-bath with silver acetate in glacial acetic acid solution, the acetylchloro-derivative of soluble starch yields Pregl's triacetyl-soluble starch (Abstr., 1902, i, 136) and a *substance* which has $[\alpha]_D$ 151°, and must contain acetyl derivatives of the decomposition products of soluble starch, as on hydrolysis it yields a substance which gives a violet coloration with iodine.

The action of acetic anhydride saturated with hydrogen chloride at −12° on glycogen at the laboratory temperature for twenty hours leads to the formation of an *acetylchloro*-compound, which contains 0·15 per cent. of chlorine and has the molecular weight, calculated 23630, observed about 25000. It is a white, amorphous substance, is readily soluble in benzene, chloroform, glacial acetic acid, ethyl acetate, or acetone, and when shaken with silver acetate in glacial acetic acid solution forms the *triacetyl* derivative, $(C_6H_7O_5Ac_3)_x$, which sinters at 165°, becomes opaque at 180°, and melts at 240°. It has $[\alpha]_D + 132·34°$, and on hydrolysis yields a substance, $(C_6H_{10}O_5)_{100}$, which has $[\alpha]_D$ 192·1°, and is more soluble than glycogen, which has $[\alpha]_D$ 196·6°.

The action of acetic anhydride saturated with hydrogen chloride at −15° on cellulose (*a*) for forty-eight hours leads to the formation of a brown, amorphous *derivative*, $(C_6H_7O_2)_{34}(OAc)_{101}Cl$, which on hydrolysis with alcoholic potassium hydroxide yields cellulose, $(C_6H_{10}O_5)_{34}$, (*b*) or for fourteen days, leads to the formation of hepta-acetylchlorocellobiose, which melts at 195° and has $[\alpha]_D + 75·21°$. Hepta-acetylchlorocellobiose, prepared from cellobiose acetate (Skraup and König, Abstr., 1902, i, 35), melts at 195° and has $[\alpha]_D + 74·87°$. When warmed with silver acetate and glacial acetic acid, it yields an *acetate*, which melts at 200°, has $[\alpha]_D - 30·05°$, and is not identical with cellobiose acetate, which melts at 228° and has $[\alpha]_D + 43·64°$. On hydrolysis with alcoholic potassium hydroxide, the acetate melting at 200° yields a brown mass, which does not deposit cellobiose on solution in water and addition of a crystal of that substance. G. Y.

Decomposition of Nitrocellulose at Temperatures below that of Ignition. ALEXIS V. SAPOSCHNIKOFF and W. JAGELLOWITSCH (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 822—828. Compare Abstr., 1904, i, 799).—The authors have determined the velocities of decomposition, at different temperatures below that of ignition, of ordinary pyroxylin having the composition $C_{24}H_{29}(NO_3)_{11}O_9$ by measuring the volumes of gas evolved in definite time intervals. The volume-time curves for temperatures from 120° to 135° are widely different in character from those obtained at 140—150°, but both exhibit points of inflexion corresponding with maximal values of *dv/dt* (v = volume of gas and t = time); the relation between these maximal velocities and the temperature is expressed by the following equations: (1) between 120° and 135°, $(dv/dt)_{\text{max.}} = -2\cdot22 + 0\cdot0192T$; (2) between 135° and 150°, $(dv/dt)_{\text{max.}} = -64\cdot22 + 0\cdot48T$. At 150°, the decomposition of the pyroxylin is represented by the equation: $C_{24}H_{29}(NO_3)_{11}O_9 = 6\cdot27CO_2 + 3\cdot58CO + 5\cdot37NO + 2\cdot71N_2 + 8H_2O + C_{14\cdot15}H_{13}O_{12\cdot5}N_{0\cdot21}$, and at 120° the products are

$$2\cdot31CO_2 + 1\cdot75CO + 2\cdot06NO + 2\cdot7N_2 + 14\cdot41H_2O + C_{19\cdot94}H_{0\cdot2}O_{19\cdot16}N_{3\cdot56}.$$

At temperatures above 135°, the solid residue contains practically no nitrogen, whilst at lower temperatures about 25—30 per cent. of the nitrogen, but very little hydrogen, remains in the undecomposed matter.

T. H. P.

Behaviour of Vegetable and Animal Textile Fibres with Solutions of Metallic Salts. W. Schellens (*Arch. Pharm.*, 1905, **243**, 617—627).—One gram of the fibre was allowed to remain for several days in 50 c.c. of the solution of the metallic salt. The total amount of salt taken up was in part merely adsorbed by the fibre; this was removed by washing and boiling with water until the wash-water no longer gave any reaction of either constituent of the salt; the amount then remaining "fixed" in the fibre was determined if possible (compare Zacharias, Abstr., 1902, i, 725). The amounts are expressed as percentages of the weight of the fibre. As a rule, it is either the base or the acid of the salt that is taken up; proportionately more is taken up out of dilute solutions as compared with strong ones, and the amount taken up is greater as the extent to which the salt is hydrolysed is greater; in no case was a coloration of the fibre observed.

With ferric chloride, the following results were obtained, in which the numbers refer to the weight of iron fixed from solutions containing 1 and 0·1 per cent. of iron respectively: cotton-wool, 0·112, 0·112; filter-paper, 0·23, 0·123; precipitated cellulose, 0·112, 0·112; woolly fibre from the seeds of *Eriodendron anfractuosum*, 1·01, 0·56; jute, 0·56, 0·44; raw silk, 0·67, 0·67; yellow Japanese silk (organsin), 0·67, 0·615; precipitated silk, 0·24; wool, 0·84, 0·36. From alcoholic ferric chloride and from aqueous ferric acetate, more iron is fixed, corresponding with the greater hydrolysis (Schaer, Abstr., 1901, ii, 603). The case of wool and ferric acetate is exceptional, however, less iron being fixed than from aqueous ferric chloride of equivalent strength. Mercury is taken up by the fibres from aqueous mercuric chloride, and also from aqueous mercuric cyanide to a smaller extent; only a small portion is fixed, however. From aqueous mercuric acetate, large quantities of mercury are taken up, amounting to 12·3 in the case of wool. Lead is also taken up from the aqueous nitrate; some of it is fixed in the case of *Eriodendron*, silk, and wool, none in the case of cotton-wool and paper. Chromium trioxide is taken up from aqueous potassium dichromate, and iodine (iodide?) from aqueous potassium iodide. Potassium nitrate in aqueous solution is reduced to nitrite or even further; in the case of silk and wool in a 0·01 per cent.

solution, neither nitrate nor nitrite could be detected after eight days, and in the first case the solution had become alkaline, not so in the other.
C. F. B.

Mixed Triammine Cobalt Salts containing Ethylenediamine and Ammonia. Alfred Werner and Ad. Grün (*Ber.*, 1905, **38**, 4033—4040. Compare Werner, *Zeit. anorg. Chem.*, 1895, **8**, 174; Jörgensen, Abstr., 1897, ii, 41, 453).—*Trinitrocobaltethylenediamineammine*, $(NO_2)_3Co(NH_3)C_2H_4(NH_2)_2$, is prepared by adding ethylenediamine to a solution of Erdmann's sodium tetranitrodiamminecobalt at 60°; it crystallises in brown leaflets or long, broad, feathery needles, is stable towards cold hydrochloric acid, but when warmed with the acid is converted into *dichloroaquocobaltethylenediamineammine chloride*, $[Cl_2(OH_2)Co(NH_3)C_2H_4(NH_2)_2]Cl$, which crystallises in small, greenish-black, slightly dichroic needles, dissolves in ice-cold water to form a green solution which becomes blue, and on dilution red; silver nitrate precipitates the total chlorine from the aqueous solution as silver chloride. When heated, the neutral, aqueous solution deposits cobalt hydroxide; hot hydrochloric acid decomposes the chloride with formation of "ethylenediamine chlorocobaltoate," which separates in blue leaflets. The action of sodium nitrite on the chloride leads to the formation of trinitrocobaltethylenediamineammine. The *nitrate*, $[Cl_2(OH_2)Co(NH_3)C_2H_4(NH_2)_2]NO_3$, is formed by treating the chloride with nitric acid of sp. gr. 1·4; it crystallises in green scales having a metallic lustre and is extremely soluble in water.

Chlorodiaquocobaltethylenediamineammine oxalate,

$$[Cl(OH_2)_2Co(NH_3)C_2H_4(NH_2)_2]C_2O_4,$$

is formed by heating the chloride of the dichloroaquo-compound with oxalic acid in aqueous alcoholic solution; it crystallises in glistening, blue leaflets, is moderately soluble in hot water, when treated with hydrochloric acid in aqueous solution yields the dichloroaquochloride from which it is formed, and gives a precipitate of calcium oxalate with calcium chloride in ammoniacal solution. It forms silver chloride only slowly with silver nitrate in aqueous solution, and when heated at 105° loses H_2O.

Chlorobromoaquocobaltethylenediamineammine bromide,

$$[ClBr(OH_2)Co(NH_3)C_2H_4(NH_2)_2]Br,$$

formed by the action of hydrobromic acid of sp. gr. 1·49 on the dichloroaquochloride, crystallises in small, olive-green needles, sinters and loses H_2O at 105°, forming a yellow crust which dissolves in water to form a yellow solution, and forms a sparingly soluble *iodide* with aqueous potassium iodide and an easily soluble, light green *nitrate* with concentrated nitric acid. When warmed with water and treated with an equal volume of hydrobromic acid of sp. gr. 1·49, it forms *dibromoaquocobaltethylenediamineammine bromide*,

$$[Br_2(OH_2)Co(NH_3)C_2H_4(NH_2)_2]Br,$$

which crystallises in small, stellate aggregates of needles, showing strong dichroism from bluish-black to brown, forms a green powder when finely divided, and dissolves in water to a brown solution.
G. Y.

Amides of α- and β-Aminopropionic Acids. Antoine P. N. Franchimont and H. Friedmann (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, 8, 475—477).—*α-Aminopropionamide*,

$$NH_2\cdot CHMe\cdot CO\cdot NH_2,$$

crystallises from alcohol in needles, is very soluble and hygroscopic and melts at 62°; it gives a crystalline *hydrochloride*, a crystalline, orange-red *platinichloride*, and a yellow *picrate* melting at 199°.

β-Aminopropionamide, $NH_2\cdot CH_2\cdot CH_2\cdot CO\cdot NH_2$, is very hygroscopic and soluble, but was purified by precipitating the methyl-alcoholic solution with ether and forms beautiful crystals melting at 41°.

Neither compound is identical with the supposed aminopropionamide isolated from urine by Baumstark in 1873. T. M. L.

Configuration of Stereoisomeric Chromium Salts. Paul Pfeiffer [with A. Trieschmann] (*Annalen*, 1905, **342**, 283—305. Compare Abstr., 1905, i, 33).—It was shown (*loc. cit.*) that two series of isomeric chromium compounds could be obtained and converted into two corresponding series of stereoisomeric oxalates by treatment with potassium oxalate. Thus, violet dichlorodiethylenediaminechromium chloride yields red crystals of an oxalate, $Cr_2(C_2O_4)_3,3En$, where En = ethylenediamine. The isomeric green salt, on the other hand, gives a violet compound, $Cr_2Cl_2(C_2O_4)_2,3En$.

A constitution for the red salt, $Cr_2(C_2O_4)_3,3En$, may be obtained by considering it as formed from any two of the complex ions, $(En_3Cr)^{\cdot\cdot\cdot}$, $(En_2CrC_2O_4)^{\cdot}$, $[EnCr(C_2O_4)_2]'$, or $[Cr(C_2O_4)_3]'''$; four formulæ are possible, $(En_3Cr)[Cr(C_2O_4)_3]$, $(En_2CrC_2O_4)[EnCr(C_2O_4)_2]$, and two formulæ which imply a double molecular weight, $(En_3Cr)[EnCr(C_2O_4)_2]_3$, and $(En_2CrC_2O_4)_3[Cr(C_2O_4)_3]$.

Since, however, the red salt reacts with concentrated hydrobromic acid yielding the oxalodiethylenediaminechromium bromide,

$$(En_2CrC_2O_4)Br,$$

identical with the salt described by Werner and Schwarz, the formulæ $(En_2CrC_2O_4)[EnCr(C_2O_4)_2]$ and $(En_2CrC_2O_4)_3[Cr(C_2O_4)_3]$ are alone possible. If the red salt is treated with potassium iodide, the insoluble oxalodiethylenediaminechromium iodide, $(En_2CrC_2O_4)I$, separates, whilst the soluble potassium dioxaloethylenediaminechromate, $[EnCr(C_2O_4)_2]K$, remains in solution, and, on adding excess of potassium iodide solution, is thrown down as the *double* salt, $[EnCr(C_2O_4)_2]K,KI,2H_2O$. These facts are in favour of the formula $(En_2CrC_2O_4)[EnCr(C_2O_4)_2]$ for the red salt.

The red salt was then synthesised from the oxalodiethylenediaminechromium bromide, $(En_2CrC_2O_4)Br$, and the potassium salt, $[EnCr(C_2O_4)_2]K$, which were mixed in concentrated aqueous solution; the red salt must therefore be called *oxalodiethylenediaminechromium dioxaloethylenediaminechromate.*

The isomeric salt, $(En_3Cr)[Cr(C_2O_4)_3]$, was obtained from triethylenediaminechromium chloride, $(En_3Cr)Cl_3$, and potassium oxalochromate, $[Cr(C_2O_4)_3]K_3$; it crystallised in green, lustrous leaflets with 6 or $7H_2O$, and was decomposed by a concentrated solution of potassium iodide into the iodide, $(En_3Cr)I_3$, and the oxalochromate, $[Cr(C_2O_4)_3]K_3$.

The violet salt, $Cr_2Cl_2(C_2O_4)_2,3En$, has an analogous constitution, $(En_2CrCl_2)[EnCr(C_2O_4)_2]$, and is *dichlorodiethylenediaminechromium dioxaloethylenediaminechromate.* With concentrated nitric acid, it yielded the green nitrate, $(En_2CrCl_2)NO_3$, and it can be synthesised from dichlorodiethylenediaminechromium chloride and potassium dioxaloethylenediaminechromate,

$$(En_2CrCl_2)Cl + [EnCr(C_2O_4)_2]K = (En_2CrCl_2)[EnCr(C_2O_4)_2] + KCl.$$

Further, the analogous violet *cobalt* salt, $(En_2CoCl_2)[EnCr(C_2O_4)_2]$, was prepared and crystallised in leaflets.

The reactions between potassium oxalate and the violet dichlorodiethylenediaminechromium salts is thus represented:

$$(En_2CrCl_2)^{\cdot} + (C_2O_4)'' = (En_2CrC_2O_4)^{\cdot} + 2Cl' ; \quad (En_2CrC_2O_4)^{\cdot} + (C_2O_4)'' = [EnCr(C_2O_4)_2]' + En ; \quad (En_2CrC_2O_4)^{\cdot} + [EnCr(C_2O_4)_2]' = (En_2CrC_2O_4)[EnCr(C_2O_4)_2].$$

The reactions between potassium oxalate and the green dichloro-salt are, on the other hand, to be represented:

$$(En_2CrCl_2)^{\cdot} + 2(C_2O_4)'' = [EnCr(C_2O_4)_2]' + 2Cl' + En ; \quad (En_2CrCl_2)^{\cdot} + [EnCr(C_2O_4)_2]' = (En_2CrCl_2)[EnCr(C_2O_4)_2].$$

In the case of both salts, the oxalo-group replaces the chlorine of the positive ion, En_2CrCl_2, in the green salt, converting it into the negative dioxalo-ion, $EnCr(C_2O_4)_2$, but in the case of the violet salt also giving the mono-oxalo-positive ion, $En_2CrC_2O_4$.

It is pointed out that all these observations are in agreement with the view that the two series of salts are stereoisomeric. K. J. P. O.

Resolution of Leucine into its Optically Active Components by means of its Formyl Derivative.

Emil Fischer and Otto Warburg (*Ber.*, 1905, **38**, 3997—4005. Compare Abstr., 1900, i, 646).—*Formyl-leucine*, $C_7H_{13}O_3N$, prepared by heating leucine repeatedly with 98·5 per cent. formic acid and washing carefully so as to remove unchanged leucine, softens at about 112° and melts at 115—116° (corr.); it crystallises from water in microscopic octahedra, and is converted by phosphorus pentachloride into a *formyl-leucyl chloride*, $C_4H_9{\cdot}CH(NH{\cdot}CHO){\cdot}COCl$, which is a colourless, indistinctly crystalline powder.

Formylglycine, $CHO{\cdot}NH{\cdot}CH_2{\cdot}CO_2H$, prepared by the action of formic acid on aminoacetic acid, crystallises from water or alcohol, softens at 149°, and melts and decomposes at 153—154° (corr.).

When formyl-leucine is heated with an alcoholic solution of brucine, the *brucine* salt of formyl-*d*-leucine separates in a nearly pure state, and, on decomposing the latter with *N*-sodium hydroxide, *formyl*-d-*leucine* is obtained; it crystallises from water in long, thin prisms, melts at 141—144° (corr.) and has $[\alpha]_D$ +18·8° at 20° in 10 per cent. alcoholic solution. *Formyl*-l-*leucine*, prepared by decomposing the more soluble brucine salt, has the same melting point as the *d*-form and $[\alpha]_D$ −18·5° at 20°.

To hydrolyse the formyl-derivatives, they are heated with 10 per cent. hydrochloric acid, the excess of hydrochloric acid and the formic acid removed by distilling under reduced pressure, and the active amino-acid separated by adding the calculated quantity of lithium hydroxide in alcoholic solution. *d*-Leucine has $[\alpha]_D$ − 15·6° at 20°, whilst *l*-leucine has $[\alpha]_D$ + 15·6° at the same temperature. These values agree fairly closely with those obtained with the active leucines prepared from the benzoyl-leucines (Fischer, *loc. cit.*), but a specimen of *l*-leucine prepared from proteids by E. Schulze had $[\alpha]_D$ + 16·9°. On the other hand, *d*-leucine obtained from the urine of a rabbit to which inactive leucine had been administered had $[\alpha]_D$ − 15·5° at 20°. If the value obtained with Schulze's product corresponds with the true active leucine, the products prepared from the formyl and benzoyl derivatives must contain about 10 per cent. of the racemic form. W. A. D.

Synthesis of Polypeptides. X. Polypeptides of the Diamino- and Hydroxyamino-acids. EMIL FISCHER and UMETARO SUZUKI (*Ber.*, 1905, **38**, 4173—4196. Compare Abstr., 1905, i, 121).—*Diaminopropionic acid dipeptide* is obtained as a tough, gummy mass with an alkaline reaction on heating the hydrochloride of the dimethyl ester with water at 80°; the *picrate* is a citron-yellow, crystalline powder, which sinters at 200° and melts and decomposes at 222° (corr.); the crystalline *hydrochloride* decomposes above 250°. Inactive *lysyl-lysine*, $C_{12}H_{26}O_3N_4$, forms a yellow, crystalline *picrate* which sinters at 170°, melts at 185° (corr.) to a bright brownish-red oil, and decomposes on further heating; the *hydrochloride* crystallises in short, twin prisms melting at about 205° (corr.). Histidine anhydride forms a *picrate* separating in stellar aggregates of citron-yellow, flat crystals, which when heated become brown at 235° (corr.) and decompose at 255° (corr.); the *hydrochloride* crystallises in thin, colourless prisms aggregated in star-like clusters, which melt and decompose at about 320° (corr.).

Histidylhistidine, $C_{12}H_{16}O_3N_6$, forms a *picrate* crystallising in citron-yellow prisms which melt at 165—175°.

Arginine methyl ester forms a citron-yellow, crystalline *picrate*, which becomes brown at 200° and melts and decomposes at about 218° (corr.), and a *nitrate* crystallising in large prisms and melting at 189° (corr.).

iso*Seryl*iso*serine methyl ester*, $C_7H_{14}O_5N_2$, forms large crystals which begin to change at 100° and are completely melted at 180°.

iso*Seryl*iso*serine* is a colourless powder which sinters at 220° and decomposes at a higher temperature; its aqueous solution has an acid reaction.

Serine methyl ester is a colourless, strongly alkaline syrup; the *hydrochloride* forms colourless, transparent, hexagonal plates melting at about 114° (corr.) and decomposing above this temperature. *Serine anhydride*, $C_6H_{10}O_4N_2$, is obtained either as microscopic, four-sided, oblique plates, which become brown at 265° (corr.) and decompose at 280° (corr.), or in long, narrow, pointed prisms melting at 226° (corr.).

Serylserine is obtained as a mixture of two isomerides; the one present in greater quantity crystallises in stellate leaflets and on heating becomes brown at 200° and decomposes at 210° (corr.). The aqueous solution is strongly acid and dissolves copper oxide to form a blue solution. The *hydrochloride* of the *ester* crystallises in star-like aggregates of pointed needles.

A method of preparing arginine from edestin is described.

E. F. A.

Action of Carbamide on Compounds of Cyanoacetic Acid.

Gustav Frerichs and L. Hartwig (*J. pr. Chem.*, 1905, [ii], **72**, 489—510).—When boiled together, carbamide and ethyl cyanoacetate interact to form an ester,  $\mathrm{CO}\genfrac{}{}{0pt}{}{<\!\!-\mathrm{N}=\!\!>}{\mathrm{NH}}\mathrm{C\cdot CH_2\cdot CO_2Et}$, which crystallises from water in long, colourless needles, melts and decomposes at 162°, has the solubility 1 : 8333 in water at 24°, and gives a blood-red coloration with traces of aqueous ferric chloride. It has acidic properties, liberates carbonic and acetic acids from their salts, and in hot aqueous solution dissolves metallic zinc with evolution of hydrogen. The *potassium*, $C_6H_7O_3N_2K,2H_2O$, *ammonium*, $C_6H_7O_3N_2NH_4$, *silver*, and *copper*, $(C_6H_7O_3N_2)_2Cu,2H_2O$, derivatives are described; the *aniline* compound, $C_6H_8O_3N_2,C_6H_7N$, crystallises in needles and melts and decomposes at 144—145°; the m-*toluidine* compound, $C_{13}H_{17}O_3N_3$, crystallises in white leaflets and melts and decomposes at 143°; the *strychnine* compound, $C_6H_8O_3N_2,C_{21}H_{22}O_2N_2$, crystallises in sheaves of flat needles and melts and decomposes at 188°. The ester does not interact with benzaldehyde, formaldehyde, or hydroxylamine; on hydrolysis with alcoholic potassium hydroxide or aqueous ammonia, it yields carbon dioxide, alcohol, ammonia, and acetic acid; when heated with 25 per cent. hydrochloric acid in a reflux apparatus, it yields pure ammonium chloride, but when warmed with dilute nitric acid, a mixture of ammonium nitrate and oxalate. With bromine in aqueous solution, it forms an unstable, oily *additive* compound, $C_6H_8O_3N_2Br_2$, which is soluble in ether and liberates iodine from potassium iodide.

The corresponding *methyl ester*,  $\mathrm{CO}\genfrac{}{}{0pt}{}{<\!\!-\mathrm{N}=\!\!>}{\mathrm{NH}}\mathrm{C\cdot CH_2\cdot CO_2Me}$, is formed by heating carbamide with methyl cyanoacetate; it crystallises from water in colourless leaflets containing $1\frac{1}{2}H_2O$, melts at 116°, or when anhydrous at 128°, gives a red coloration with aqueous ferric chloride, and is slightly more soluble than the ethyl ester, which it resembles in its chemical properties. The *potassium*, $C_5H_5O_3N_2K$, *ammonium*, $C_5H_5O_3N_2NH_4$, and *copper*, $(C_5H_5O_3N_2)_2Cu,\frac{1}{2}H_2O$, derivatives are described; the *aniline* compound, $C_5H_6O_3N_2,C_6H_7N$, crystallises in white leaflets and melts at 120°; the m-*toluidine* compound, $C_{12}H_{15}O_3N_3$, forms sheaves of slender needles and melts and decomposes at 120—121°; the *strychnine* compound, $C_{26}H_{28}O_5N_4$, crystallises in flat, white needles and melts and decomposes at 211°. The methyl ester forms an unstable bromine derivative similar to that obtained from the ethyl ester.

G. Y.

Mercuric Oxycyanide. KARL HOLDERMANN (*Arch. Pharm.*, 1905, **243**, 600—617. Compare Holdermann, Abstr., 1904, i, 301, and Richard, *J. Pharm. Chim.*, 1903, **18**, 553).—By dissolving mercuric oxide in aqueous mercuric cyanide and crystallising the solution fractionally, it was shown that only one oxycyanide is formed; this has the composition $Hg(CN)_2,HgO$. It is never possible to convert mercuric cyanide quantitatively into this compound; the most convenient method of separation is to mix the cyanide and oxide in equivalent proportions and moisten the mixture with a little water in a conical flask; heat the mixture for four hours on the water-bath, replacing the water as it evaporates; extract the mass with boiling water (500 c.c. for 13·5 grams of cyanide and 11·5 grams of oxide); filter the solution, and allow it to crystallise; in these circumstances, about 80 per cent. of the cyanide is obtained as oxycyanide.

The amount of oxide in a sample of mercuric oxycyanide can be determined very readily and accurately by adding sodium chloride to a solution of the sample and titrating the oxide with *N*/10 hydrochloric acid with methyl-orange as indicator. Commercial oxycyanide contains but a small proportion of oxide.

The pure oxycyanide in aqueous solution gives no yellow coloration with potassium iodide, but an almost colourless, crystalline precipitate which dissolves in excess of the aqueous potassium iodide forming a colourless solution. Its electrolytic conductivity is even less than that of mercuric cyanide. The antiseptic action ascribed to it has been observed with very impure samples, and may not belong to the pure substance at all.

Methods of analysing samples of mercuric oxycyanide and tabloids containing it and sodium hydrogen carbonate are described in detail.

C. F. B.

Blue Iron-cyanogen Compounds and the Cause of their Colour. III. KARL A. HOFMANN and F. RESENSCHECK (*Annalen*, 1905, **342**, 364—374. Compare Abstr., 1905, i, 756).—It has been shown (*loc. cit.*) that the blue iron-cyano-compounds, formed either from ferric salts and ferrocyanides or ferrous salts and ferricyanides, are to be regarded as derivatives of potassium ferrocyanide in which potassium is either wholly or partly replaced by tervalent iron. The substances obtained on oxidising the compounds formed from ferrous salts and ferrocyanides do not belong to this class. The material so prepared from potassium ferrocyanide and a ferrous salt in molecular proportions in acid solution is quite different from the soluble Prussian blue, but identical with Williamson's violet,

$$\{Fe''(CN)_6\}Fe'''K,nH_2O,$$

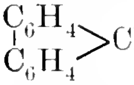
which is produced on oxidation of the residue, $\{Fe''(CN)_6\}Fe''K_2$, left in the preparation of hydrocyanic acid.

A third blue *compound*, $\{Fe(CN)_6\}FeK,H_2O$, isomeric with Williamson's violet, is formed when molecular proportions of a ferrous salt and potassium ferrocyanide are brought together in neutral solution at the ordinary temperature and then oxidised with hydrogen peroxide. It has up to the present been confused with the soluble Prussian blue; it has a greenish-blue colour in aqueous solution, is stable towards a 5 per cent. solution of ammonium carbonate, but rapidly decomposed by 4 per cent. ammonia. It is completely insoluble in oxalic acid and in aqueous solution is converted by dilute sulphuric acid into an insoluble blue compound. The constitutional formula, $\{Fe''(CN)_6\}(Fe'''OH)KH$, is suggested for this compound.

The cause of the colour of the iron-cyanogen compounds is discussed; it is pointed out that the colour is associated with the presence of both bivalent and tervalent iron in the same molecule. Similarly, red lead contains both bivalent and tervalent lead; and the deep indigo-blue sulphur sesquioxide, although the other oxides of sulphur are colourless, also contains sulphur, showing two degrees of valency. This peculiar relation between constitution and colour will be discussed in a later communication. K. J. P. O.

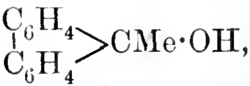
Some Derivatives of Octahydroanthracene and Perhydroanthracene. Marcel Godchot (*Compt. rend.*, 1905, **141**, 1028—1030. Compare Abstr., 1904, i, 987; 1905, i, 201).—*Hexahydroanthrone oxime*, $C_{14}H_{16}\!:\!N{\cdot}OH$, obtained by heating hexahydroanthrone and hydroxylamine acetate, crystallises from alcohol in small, colourless needles melting at 143°, readily soluble in alcohol, ether, or light petroleum, and reduced by sodium in alcoholic solution to *octahydroanthramine*, $C_{14}H_{17}{\cdot}NH_2$, a yellow liquid boiling at 182° under 12 mm. pressure and having strongly basic properties, combining with the carbon dioxide of the air; the *hydrochloride*, $C_{14}H_{17}{\cdot}NH_2,HCl$, forms colourless prisms decomposing without fusion at 188° and readily soluble in water or alcohol; the *picrate* forms yellow needles melting at 212°, readily soluble in alcohol, less so in ether or light petroleum; the *acetyl* derivative, $C_{14}H_{17}{\cdot}NHAc$, crystallises from alcohol in beautiful colourless needles melting at 183°, and soluble in benzene, ether, or chloroform. Perhydroanthracene, $C_{14}H_{24}$, prepared by reducing anthracene with hydrogen iodide and phosphorus (compare Lucas, Abstr., 1888, 1201), can be obtained more readily by the action of hydrogen iodide and red phosphorus on octahydroanthracene in sealed tubes at 250° or by the direct hydrogenation of octahydroanthracene in the presence of reduced nickel at 180°, a liquid hydrocarbon, probably *dodecahydroanthracene*, $C_{14}H_{22}$, being formed at the same time. M. A. W.

Fluorene Compounds. Fritz Ullmann and R. von Wurstemberger (*Ber.*, 1905, **38**, 4105—4110).—9 : 9-*Diphenylfluorene* [*diphenylbiphenylenemethane*],



$\left.\begin{array}{l}C_6H_4\\ \,|\\ C_6H_4\end{array}\right>CPh_2$, prepared by the action of bromobenzene and magnesium on methyl diphenyl-2-carboxylate, crystallises from acetic acid in colourless prisms, melts at 222° (corr.), and boils without decomposition above 400°.

Biphenylenemethylcarbinol [*9-methylfluorene alcohol*],

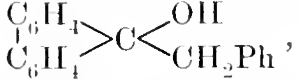


$\left.\begin{array}{l}C_6H_4\\ \,|\\ C_6H_4\end{array}\right>CMe{\cdot}OH$, prepared by the action of methyl iodide and magnesium on fluorenone, crystallises from benzene in glistening prisms and melts at 174·5°.

The corresponding *ethyl* compound, $\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!>\!\mathrm{CEt{\cdot}OH}$, crystallises from light petroleum and melts at 101°.

Biphenylenepropylene [*9-ethylidenefluorene*], $\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!>\!\mathrm{C{:}CHMe}$, prepared by the action of acetic and hydrochloric acids on the preceding compound, crystallises from acetic acid and melts at 104°.

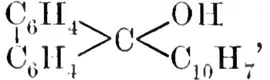
Biphenylenebenzylcarbinol [*9-benzylfluorene alcohol*],



$$\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!>\!C\!<\!\begin{matrix}OH\\ \\ CH_2Ph\end{matrix},$$

separates from a mixture of benzene and light petroleum in large crystals and melts at 139°. *Biphenylenephenylethylene* [*9-benzylidenefluorene*], $\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!>\!\mathrm{C{:}CHPh}$, separates as a yellow oil which crystallises and melts at 76°.

Biphenylene-a-naphthylcarbinol [*9-a-naphthylfluorene alcohol*],



$$\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!>\!C\!<\!\begin{matrix}OH\\ \\ C_{10}H_7\end{matrix},$$

crystallises from a mixture of benzene and light petroleum and melts at 151·5°. It is reduced by zinc and acetic acid to *biphenylene-a-naphthylmethane* [*9-a-naphthylfluorene*], $C_{23}H_{16}$, which separates from alcohol in colourless needles and melts at 103·5°. *Biphenylene*-p-*aminophenyl-a-naphthylmethane* [*9-*p*-aminophenyl-9-a-naphthylfluorene*], $\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!>\!C\!<\!\begin{matrix}C_6H_4{\cdot}NH_2\\ \\ C_{10}H_7\end{matrix}$, prepared by the action of aniline on the carbinol, separates from alcohol in small, white, strongly electric crystals and melts at 145°. The *hydrochloride*, $C_{29}H_{21}N,HCl$, is a white, crystalline powder and melts and decomposes at 225—230°.

T. M. L.

Acetylene Linking. FRITZ STRAUS (*Annalen*, 1905, **342**, 190—265).—Phenylacetylene, together with copper phenylacetylide and diphenyldiacetylene, are formed when copper phenylpropiolate,

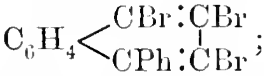
$$(\mathrm{CPh{:}C{\cdot}CO_2})_2\mathrm{Cu},4\mathrm{H_2O},$$

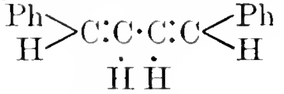
is heated. Solutions of sodium phenylpropiolate and cupric chloride are mixed and steam passed into the mixture, when the hydrocarbon distils over. If copper phenylpropiolate is treated with pyridine or quinoline, only copper phenylacetylide and diphenyldiacetylene are formed.

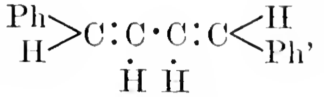
Copper phenylacetylide dissolves in boiling acetic acid with an orange-yellow coloration, no appreciable quantity of hydrocarbon being evolved. The solution deposits on cooling or on addition of ice-cold water, the *double salt*, $\mathrm{CPh{:}CCu,CH_3{\cdot}CO_2Cu}$, which crystallises in orange-yellow leaflets; this substance oxidises very readily, its solution in organic solvents being decomposed by contact with air, copper phenylacetylide being formed. If air is passed through its boiling solution in acetic acid, diphenylbuteninene is formed, a reaction which is thought to indicate the presence of more than one hydrocarbon radicle in the molecule of the copper compound.

Diphenyldiacetylene, $CPh{:}C{\cdot}C{:}CPh$, is prepared by treating copper phenylacetylide with an aqueous solution of potassium ferricyanide made alkaline by potassium hydroxide, or by warming copper phenylpropiolate with pyridine ; it is crystallised from methyl alcohol and melts at 86—87°. *Diphenylbuteninene*, $CHPh{:}CH{\cdot}C{:}CPh$, prepared by dissolving copper phenylacetylide in acetic acid in a flask from which the air has been expelled, boiling, and then sucking air through the mixture, crystallises in colourless prisms melting at 96·5—97°. The solution in acetic acid becomes blue on the addition of sulphuric acid, and then forms a dichroic, violet-red liquid.

[With Rudolf Müller.]—In chloroform or carbon disulphide solution, diphenyldiacetylene yields a mixture of stereoisomeric tetrabromides, $CPhBr{:}CBr{\cdot}CBr{:}CPhBr$, from which the hydrocarbon is regenerated by reduction with zinc dust in acetone solution. It is noteworthy that more than four atoms of bromine cannot be added to the molecule. A *dibromide*, $CPhBr{:}C{:}C{:}CPhBr$ (?), is formed as an intermediate product, crystallising in yellow rhombs, melting at 142°. The mixture of tetrabromides melts at 120—140°, and a *tetrabromide* (m. p. 172°) can be isolated from this mixture by crystallisation from petroleum.

When diphenyldiacetylene in acetic acid is treated with excess of bromine, a *tribromo*-derivative is obtained which is not, as Hollemann thought, a tribromo-derivative of the diacetylene, but tribromo-α-phenylnaphthalene,  $C_6H_4<\begin{matrix}CBr{:}CBr\\ |\\ CPh{:}CBr\end{matrix}$; it crystallises in yellow nodules melting at 151°. When reduced with alcohol and sodium amalgam, it is converted into α-phenylnaphthalene, $C_{10}H_7Ph$, which boils at 192—195° under 17 mm. pressure and is oxidised by potassium dichromate and sulphuric acid to *o*-benzoylbenzoic acid. Reduction of the tribromide with zinc dust and acetic acid yields a *dibromo-α-phenylnaphthalene*, $C_{10}H_5Br_2Ph$, which forms crystals melting at 111—111·5°.

Diphenyldiacetylene is reduced by boiling in alcoholic solution with zinc dust, light being carefully excluded, to the labile cis-cis-*diphenylbutadiene*,  $\begin{matrix}Ph\\H\end{matrix}>C{:}\underset{H}{C}{\cdot}\underset{H}{C}{:}C<\begin{matrix}Ph\\H\end{matrix}$, which crystallises in leaflets or four-sided plates melting at 70—70·5°; when exposed to sunlight, this hydrocarbon is transformed into the stable trans-trans-*diphenylbutadiene*, which melts at 142—145°, or when pure at 150—151°. As an intermediate product in the reduction, cis-*diphenylbuteninene*,  $\begin{matrix}Ph\\H\end{matrix}>C{:}C<\begin{matrix}C{:}CPh\\H\end{matrix}$, is formed ; it is a yellow oil, freezing at about 0° and boiling at 187·5—188° under 12 mm. pressure ; when exposed to sunlight, it is transformed into the stable *trans*-diphenylbuteninene (m. p. 97°) above described. The *cis*-diphenylbuteninene forms with bromine a mixture of tetrabromides from which needles melting and decomposing at 205°, leaflets melting at 135—136°, and prisms melting and decomposing at 160° can be isolated. The two isomerides with higher melting points are probably identical with the compounds obtained from *trans*-diphenylbuteninene. On treatment with hydrogen bromide, the same compound is obtained from both the *cis*- and *trans*-isomerides.

cis-trans-*Diphenylbutadiene*,  $^{Ph}_{H}{>}C{:}\underset{H}{C}\cdot\underset{H}{C}{:}C{<}^{H}_{Ph}$, is prepared from *trans*-diphenylbuteninene by reduction with zinc copper couple in alcohol solution in the absence of sunlight, and crystallises in leaflets melting at 150—151°. It is the most unstable of the diphenylbutadienes and passes on transitory exposure to light into the stable *trans-trans*-form.

On bromination, *cis-cis*-diphenylbutadiene yields in chloroform solution a mixture of tetrabromides from which two *compounds* can be isolated, one crystallising in leaflets melting at 225° and a second crystallising in prisms melting and decomposing at 180°.

trans-Diphenylbuteninene yields a *tetrabromide*,

$CBrPh{:}CBr\cdot CHBr\cdot CHBrPh$,

when brominated in chloroform solution, which crystallises in leaflets melting and decomposing at 197°; at the same time, a second tetrabromide is formed melting and decomposing at 157—158°. Hydrogen bromide converts the *trans*-diphenylbuteninene into *diphenylbutadiene dibromide*, $C_{16}H_{14}Br_2$, which crystallises in needles melting and decomposing at 142°, and a *bromodiphenylbutadiene*, $C_{16}H_{13}Br$, which crystallises in needles melting at 113·5—114°; the latter monobromo-derivative is not changed by hydrogen bromide and is converted by bromine into *bromodiphenylbutadiene dibromide*, $C_{16}H_{13}Br_3$, crystallising in needles melting at 145—147°.

All the diphenylbutadiene bromides are reduced by zinc dust or the zinc copper couple to the stable *trans-trans*-diphenylbutadiene (m. p. 150—151°).

Δ^2-*Diphenylbutene*, $CH_2Ph\cdot CH{:}CH\cdot CH_2Ph$, prepared from diphenylbutadiene, crystallises in needles melting at 45—45·5° and yields a dibromide which, by heating with quinoline, is converted into diphenylbutadiene. When oxidised with potassium permanganate at 0°, *βγ-dihydroxy-αδ-diphenylbutane*, $CH_2Ph\cdot CH(OH)\cdot CH(OH)\cdot CH_2Ph$, is obtained as needles melting at 125°. The diphenylbutene can also be prepared by reducing with alcohol and sodium amalgam diphenyldiacetylene, *trans*-diphenylbuteninene, *trans-trans*-diphenylbutadiene, and *cis-cis*-diphenylbutadiene.

Δ^2-Phenylbutene, $CH_2Ph\cdot CH{:}CHMe$, is formed from phenylbutadiene by reduction with sodium amalgam and alcohol, but styrene is not reduced under similar treatment. Phenylacetylene is reduced by zinc dust and alcohol to styrene and diphenylbutadiene; with zinc dust and acetic acid, diphenyldiacetylene yields a number of reduction products. Tolane is not attacked by sodium amalgam and alcohol, but by zinc dust and alcohol is converted into *iso*stilbene. When oxidised, stilbene yields *iso*hydrobenzoin, and *iso*stilbene, benzoin.

K. J. P. O.

Action of Ethylene Dibromide on *p*-Nitrosodialkylanilines. II. Henry A. Torrey (*Amer. Chem. J.*, 1905, 34, 475—481. Compare Abstr., 1902, i, 755).—Di-*p*-nitrosodimethylaniline-ethylene, obtained by the action of ethylene dibromide on *p*-nitrosodimethylaniline, is identical with tetramethyldiaminoglyoxime *N*-phenyl ether, described by Pechmann and Schmitz (Abstr., 1898, i, 309). When the reaction takes place in alcoholic solution, tetramethyldiaminoazoxybenzene is produced. By the action of dilute nitric acid on tetraethyldiaminoglyoxime *N*-phenyl ether, tetramethyldiaminoglyoxaldianil is formed, which, when boiled with an alcoholic solution of salicylaldehyde, is converted into *o*-hydroxybenzylidene-*p*-aminodimethylaniline; whilst by the action of benzoyl chloride, benzoyl-*p*-aminodimethylaniline is produced. The dianil yields a bronze-coloured *picrate*, gives a blue precipitate with mercuric chloride, and a blue coloration with dilute solutions of bromine, chlorine, hydrochloric acid, and acyl chlorides.

By the action of ethylene dibromide on *p*-nitrosodiethylaniline, tetraethyldiaminoglyoxime *N*-phenyl ether (Pechmann and Schmitz, *loc. cit.*) and *p*-nitrosodiethylaniline hydrobromide are produced.

E. G.

New Derivatives of Pentabasic Phosphoric Acid, $P(OH)_5$. PAUL LEMOULT (*Compt. rend.*, 1905, **141**, 1241—1244).—The phosphorus alkyloxytetra-anilides of the type $P(OR^1)(NHR)_4$, where R^1 and R represent alkyl and aryl radicles respectively (compare Abstr., 1904, i, 807), condense with acetic or propionic acids to form compounds of the type $COR^1{\cdot}O{\cdot}P(NHR)_4$, which may be regarded as the acetates or propionates of the base $OH{\cdot}P(NHR)_4$. These compounds form well-defined crystals, usually containing acid of crystallisation, which they lose at 100°; they are readily decomposed by water or alkalis to form the corresponding phosphoryltrianilides, $PO(NHR)_3$, and by hydrochloric acid to form the corresponding chlorotetra-anilides.

The *o-toluidine-compound*, $OAc{\cdot}P(NH{\cdot}C_6H_4Me)_4,AcOH$, forms beautiful, colourless crystals melting at 221°. The *compound*,

$$COEt{\cdot}O{\cdot}P(NH{\cdot}C_6H_4Me)_4,EtCO_2H,$$

forms small crystals melting at 203°. The *compound*,

$$CH_2Cl{\cdot}CO{\cdot}O{\cdot}P(NH{\cdot}C_6H_4Me)_4,$$

forms a confused crystalline mass. The 1 : 3 : 4-*xylidine-compound*, $OAc{\cdot}P(NH{\cdot}C_6H_3Me_2)_4,1{\cdot}5AcOH$, forms beautiful, colourless spangles several millimetres in dimensions, melting at 210°. The *compounds*, $OAc{\cdot}P(NHPh)_4$ and $COEt{\cdot}O{\cdot}P(NHPh)_4$, obtained by the action of acetic or propionic acid respectively on trianilinephenylphosphimide, $P(NHPh)_3{:}NPh$ (Abstr., 1903, i, 672), crystallise from a mixture of benzene and ether and melt at 206—207° and 240° respectively.

M. A. W.

Partial Reduction of Aromatic Dinitro- and Polynitro-derivatives by Electrolytic Methods. KURT BRAND (*Ber.*, 1905, **38**, 4006—4015).—*m*-Nitrophenylhydroxylamine can be easily obtained by the electrolytic reduction of *m*-dinitrobenzene in an approximately neutral solution; the cathode cell consists of a porous pot containing the *m*-dinitrobenzene dissolved in aqueous alcohol with a little acetic acid and sodium acetate. The anode liquid used is 20 per cent. sulphuric acid. The cathode is made of silver gauze and the anode is a perforated lead plate.

m-*Nitrophenylhydroxylamine*, $NO_2\cdot C_6H_4\cdot NH\cdot OH$, prepared in this way, separates from hot benzene in thick, yellow crystals, melts at 118—119°, and is easily oxidised by alcoholic ferric chloride to *m*-nitronitrosobenzene (Bamberger and Hübner, Abstr., 1904, i, 115); when warmed with dilute sulphuric acid, *m*-nitrophenylhydroxylamine is converted into 2-nitro-4-aminophenol. The substance melting at 178°, described by Wohl (D.R.-P. 84138) as *m*-nitrophenylhydroxylamine, seems to be a transformation product of the latter; its nature is being investigated.

On reducing *m*-dinitrobenzene in alkaline solution, using mercury as the cathode so as to prevent the formation of a solid film on the latter and thus stopping the action, *m*-dinitroazoxybenzene is obtained; the yield is good and the method can be used for preparing the substance. The reduction of *m*-dinitrobenzene in strongly acid solution gives *m*-nitroaniline, the yield being good. W. A. D.

Hydrogenation Derivatives of Carvacrol. LÉON BRUNEL (*Compt. rend.*, 1905, **141**, 1245—1247. Compare Abstr., 1904, i, 158).—When carvacrol is directly hydrogenated in the presence of reduced nickel at 160°, a mixture of two isomeric hexahydrocarvacrols (α- and β-carvacromenthols) is produced; they are probably the two stereoisomerides formed by the hydrogenation of an intermediate ketone, the corresponding carvacromenthone (compare Abstr., 1905, i, 197, 363); when the hydrogenation is effected at 115—120°, β-carvacromenthol is the only product.

α-*Carvacromenthol* is a colourless, oily liquid with an odour of thyme, and boils at 219°.

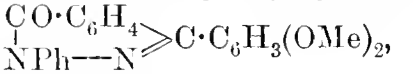
β-*Carvacromenthol*, an oily, colourless liquid with an odour of mint, boils at 222°, does not crystallise at – 10°, has a sp. gr. 0·918 at 0°, and forms well-defined esters with acids. The *formate*, $HCO_2\cdot C_{10}H_{19}$, obtained by the direct action of formic acid and the alcohol in the cold, is a colourless, mobile liquid with an agreeable odour like that of camphor, boils at 229°, and has a sp. gr. 0·954 at 0°. The *acetate*, $OAc\cdot C_{10}H_{19}$, prepared by heating acetic acid and the alcohol in sealed tubes at 130°, is a colourless, mobile liquid with a strong odour, which boils at 231·5°, does not crystallise at – 10°, and has a sp. gr. 0·933 at 0°. The *acid succinate*, $CO_2H\cdot C_2H_4\cdot CO_2\cdot C_{10}H_{19}$, prepared by heating the alcohol with succinic anhydride at 100°, crystallises from light petroleum in thin, colourless, odourless needles melting at 74° and soluble in dilute alkali solutions. The *acid phthalate*,

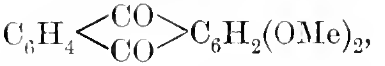
$$CO_2H\cdot C_6H_4\cdot CO_2\cdot C_{10}H_{19},$$

crystallises from alcohol in large, colourless, odourless crystals melting at 136° and soluble in alkali solutions. M. A. W.

Action of Phosphorus Pentachloride on β-Naphthol. E. BERGER (*Compt. rend.*, 1905, **141**, 1027—1028).—At temperatures below 130°, phosphorus pentachloride reacts with β-naphthol to form β-dinaphthyl ether, but when the temperature is raised to 135—140° and the heating continued for twenty-four hours, a mixture in the proportion $3PCl_5 : 2C_{10}H_7 \cdot OH$ yields 30 per cent. of β-chloronaphthalene (compare Cleve, Abstr., 1876, ii, 81; Rimarenko, Abstr., 1876, ii, 297), together with small quantities of 1:2-, 2:4-, 2:6-, and 2:8-dichloronaphthalenes, ββ-dinaphthylene oxide, and di-β-naphthyl hydrogen phosphate, melting at 143°. M. A. W.

2:3-Dihydroxyanthracene. Kasimir Lagodzinski (*Annalen*, 1905, **342**, 90—111. Compare this vol., i, 98).—2:3-Dihydroxyanthracene, which has been prepared in order to procure 2:3-anthraquinone, is obtained from the dimethyl ether of hystazarin, which is synthesised from veratrole.

o-3′:4′-*Dimethoxybenzoylbenzoic acid*, $C_6H_3(OMe)_2 \cdot CO \cdot C_6H_4 \cdot CO_2H$, prepared by warming a carbon disulphide solution of veratrole with phthalic anhydride and aluminium chloride, crystallises in colourless leaflets melting at 233° and is soluble in concentrated sulphuric acid with a blood-red coloration; the *ammonium* salt forms white needles and the *silver* salt white crystals. The acid does not react with hydroxylamine, but with phenylhydrazine yields 2-*phenyl*-4-*veratrylphthalazone*,  $\begin{matrix} CO \cdot C_6H_4 \\ | \\ NPh - N \end{matrix} > C \cdot C_6H_3(OMe)_2$, which crystallises in yellow needles melting at 189°.

The *dimethyl ether* of hystazarin (2:3-*dimethoxyanthraquinone*),  $C_6H_4 < \begin{matrix} CO \\ CO \end{matrix} > C_6H_2(OMe)_2$, is formed when dimethoxybenzoylbenzoic acid is warmed with concentrated sulphuric acid, and crystallises in golden-yellow needles melting at 237°; it yields a blood-red solution in sulphuric acid. Prolonged heating at 100° with sulphuric acid converts the dimethyl ether into the *monomethyl ether*, $OH \cdot C_{14}H_6O_2 \cdot OMe$, which crystallises in orange-yellow leaflets melting at 236°. The complete hydrolysis of the ether to hystazarin is best effected by heating with hydrobromic acid of sp. gr. 1·49 under pressure at 180°. On reduction with zinc dust and 5 per cent. ammonia, the dimethyl ether of hystazarin is converted into 2:3-*dimethoxyanthracene*, $C_{14}H_8(OMe)_2$, crystallising in colourless leaflets or needles melting at 204°; the alcoholic solution has a blue fluorescence, and the solution in sulphuric acid an orange-yellow coloration; the *picrate* is dark brown in colour; in acetic acid solution it is converted into a *polymeride* melting at 314°, and in alcoholic solution it is oxidised to the corresponding anthraquinone. When warmed with hydriodic acid (b. p. 127°), the dimethoxyanthracene yields 2:3-*dihydroxyanthracene*, which crystallises in straw-yellow leaflets decomposing at 180—192°. 2:3-*Diacetoxyanthracene* forms pale yellow crystals melting at 155—160°.

Attempts to oxidise this dihydroxyanthracene to the corresponding 2:3-dihydroxyanthraquinone were not successful.

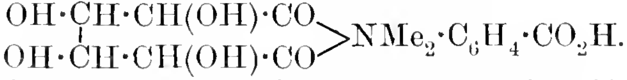
When dimethoxyanthracene is heated in acetic acid solution with hydriodic acid of sp. gr. 1·70, a *compound*, $C_{30}H_{20}O_4$, of unknown constitution is formed; it crystallises in yellow leaflets decomposing at about 260°. It forms in sulphuric acid an orange-yellow solution which becomes blood-red on heating; its solution in alkali hydroxides is yellow. It can be methylated by methyl sulphate and potassium hydroxide and acetylated by acetic anhydride. With ether, it forms the *compound*, $C_{30}H_{20}O_4,2OEt_2$, which crystallises in greenish-yellow plates. K. J. P. O.

Aromatic Sulphine Bases. FRIEDRICH KEHRMANN and A. DUTTENHÖFER (*Ber.*, 1905, **38**, 4197—4199).—The *platinichloride* of diphenylmethylsulphine, $(C_{13}H_{13}S)_2PtCl_6$, forms a yellowish-white, crystalline precipitate melting at 169·5°; the *dichromate* separates as a yellow, flocculent precipitate which rapidly becomes green and decomposes, forming a substance crystallising in orange needles and melting at 129°. *Di-α-naphthylmethylsulphine platinichloride*, $(C_{21}H_{17}S)_2PtCl_6$, forms a flesh-coloured powder and melts at 162—163°; the *aurichloride* is yellow and the *dichromate* is orange. *Di-β-naphthylmethylsulphine platinichloride* melts at 136—146°. E. F. A.

Behaviour of Esters of Organic Acids when heated with Orthophosphoric Acid. PAUL N. RAIKOW and P. TISCHKOW (*Chem. Zeit.*, 1905, **29**, 1268—1273).—The combined action of heat and orthophosphoric acid on the methyl esters of various organic acids was studied with the object of determining whether or not the ester lost carbon dioxide, leaving the methyl group attached to the rest of the molecule. The acid used was first dehydrated by heating 60 c.c. of syrupy phosphoric acid of sp. gr. 1·7 to 200° in a round-bottomed flask of 200 c.c. capacity; after cooling to below 100°, a measured quantity of the ester was added and the mixture was then boiled over iron gauze. The flask was attached to a reflux condenser, the upper end of which was connected by an india-rubber tube to one limb of a U-tube containing 50 c.c. of concentrated sulphuric acid; the other limb was connected to an apparatus for determining the amount of carbon dioxide evolved by measuring the water which it displaced from a wide-mouthed bottle of 2 litres capacity filled with water. The boiling was continued until the evolution of gas had ceased. The gas remaining in the bottle was examined for carbon dioxide and carbon monoxide; the object of the U-tube with strong sulphuric acid was to absorb any dimethyl ether which might be formed. The following compounds were examined in this way. The methyl esters of benzoic, *o*-, *m*-, and *p*-toluic, *o*-, *m*-, and *p*-chlorobenzoic, *p*-bromobenzoic, *o*-iodobenzoic, *o*-, *m*-, and *p*-aminobenzoic, *o*-, *m*-, and *p*-nitrobenzoic, salicylic, *m*- and *p*-hydroxybenzoic, 2-hydroxy-3-methylbenzoic, 2-hydroxy-4-methylbenzoic, 2-hydroxy-5-methylbenzoic, 2:4-dihydroxybenzoic, gallic, anisic, vanillic, 3-chloro-2-nitrobenzoic, 3 : 5-di-iodo-2-hydroxybenzoic, 6-nitro-2-hydroxybenzoic, 4-nitro-2-hydroxybenzoic, phthalic, *iso*phthalic, tetrachlorophthalic, *o*- and *p*-nitrophthalic, α- and β-naphthoic, *p*-hydroxynaphthoic, phenylacetic, hydrocinnamic, and cinnamic acids; also the ethyl esters of propionic and butyric acids, the phenyl esters of benzoic and salicylic acids, as well as the following two free acids, terephthalic and dichlorophthalic. The following conclusions are drawn from the experimental results:—(1) Except in the case of methyl *p*-chlorobenzoate, the methyl of the ester group was never observed to replace the $-CO_2Me$ group, and the method is therefore of no use for the introduction of a methyl group into the benzene nucleus. (2) The methyl group was commonly split off in the form of dimethyl ether; in the case of aromatic hydroxy-acids it frequently wandered from the carboxyl group to the phenolic hydroxyl group in the ortho- or para-position. The ethyl group was split off from the two ethyl esters examined in the form of ethylene. (3) With the exception of the esters of cinnamic and *o*-nitrocinnamic acids, no esters containing the $-CO_2Me$ group attached to an aliphatic complex gave off carbon dioxide. (4) The introduction of substituting groups into benzoic acid reduces the stability of the $-CO_2Me$ group. (5) The stability of the $-CO_2Me$ group is influenced both by the nature of the substituting group and by its position in the ring. (6) The hydroxyl and the amino-groups have the greatest influence. (7) In naphthoic acids, the second benzene ring acts on the $-CO_2Me$ like a substituting group, but exerts a greater influence in the case of the α- than in the case of the β-acid. (8) Unlike all other substituting groups, the introduction of a second $-CO_2Me$ increases the stability of the CO_2Me group.

P. H.

The Glucoside Structure of Conjugated Glycuronic Acids. Hermann Hildebrandt (*Beitr. chem. Physiol. Path.*, 1905, **7**, 438—454. Compare Abstr., 1901, ii, 614; Neuberg and Neimann, 1905, i, 412).—Emulsin has no action on the glycuronic acid derivative of *p*-dimethylaminobenzoic acid; the derivative probably has not a glucosidic structure and the following formula is suggested:



$$\left.\begin{array}{l}\mathrm{OH\cdot CH\cdot CH(OH)\cdot CO}\\ \quad\ \ | \\ \mathrm{OH\cdot CH\cdot CH(OH)\cdot CO}\end{array}\right>\mathrm{NMe_2\cdot C_6H_4\cdot CO_2H.}$$

p-Benzobetaine does not couple with glycuronic acid in the animal system; the greater part is eliminated unaltered and a small portion is converted into mono- and di-methyl-*p*-aminobenzoic acids.

The glucosides of glycerol and benzyl alcohol (E. Fischer, Abstr., 1895, i, 6) are hydrolysed by both emulsin and yeast.

Glycuronic acid itself is decomposed by yeast or zymase, volatile acids are formed, and the solution loses its reducing properties.

When syringinaldehyde is administered to dogs, both free syringic acid and its compound with glycuronic acid are found in the urine.

When syringin is injected subcutaneously in dogs, Körner's glucosyringic acid (Abstr., 1889, 159) and syringaglycuronic acid are found in the urine. Both acids are hydrolysed by emulsin. When coniferin is administered in the same way, no free vanillic acid can be found in the urine, but potassium vanillinglycuronate can be isolated. This is hydrolysed by emulsin.

J. J. S.

Oxidation of 4-Nitro-6-amino-*m*-xylene. Giorgio Errera and Raffaele Maltese (*Gazzetta*, 1905, **35**, ii, 370—383).—When oxidised with potassium permanganate, 4-nitro-6-diacetylamino-*m*-xylene yields a mixture of 4-nitro-6-amino*iso*phthalic acid, 4-nitro-6-amino-*m*-toluic and 6-nitro-4-amino-*m*-toluic acids and their monoacetyl derivatives.

6-*Nitro*-4-*acetylamino*-m-*toluic acid*, $C_{10}H_{10}O_5N_2$, separates from alcohol or ethyl acetate in sulphur-yellow, triclinic crystals [$a:b:c = 1\cdot6623:1:1\cdot0340$; $\alpha = 79°40'$, $\beta = 64°4'$, and $\gamma = 105°33'$], melts and decomposes at 223—225°, and dissolves slightly in water, benzene, or xylene, readily in acetic acid. The corresponding *potassium* salt was prepared and analysed.

4-*Nitro-6-acetylamino*-m-*toluic acid*, $C_{10}H_{10}O_5N_2$, crystallises from alcohol in pale straw-yellow plates melting and decomposing at 254—255° and is less soluble than the acid just described in all solvents except water; its *potassium* salt was analysed.

6-*Nitro-4-amino*-m-*toluic acid*, $C_8H_8O_4N_2$, separates from alcohol or ethyl acetate in shining, red crystals melting and decomposing at 239—240° and dissolves slightly in water or benzene.

4-*Nitro-6-amino*-m-*toluic acid*, $C_8H_8O_4N_2$, crystallises from water in golden-yellow needles which, on rapid heating in a capillary tube, melt at about 235°; it dissolves readily in alcohol or ethyl acetate and slightly in benzene. On heating the acid or its acetyl derivative with concentrated sulphuric acid, it yields 4-nitro-*o*-toluidine. The *methyl* ester, $C_9H_{10}O_4N_2$, separates from methyl alcohol in either needles or hard crystals of a pale yellowish-grey colour, and melts at 169°.

4-o-p-*Dinitroanilino*-6-*nitro*-m-*toluic acid*, $C_{14}H_{10}O_8N_4$, crystallises from acetic acid in yellow needles which melt, after blackening, at 298°; it is only slightly soluble in the ordinary solvents and gives red salts.

1 : 3 : 8-*Trinitro-7-methylacridone*, $C_{13}NH_5Me(NO_2)_3$, prepared by heating the preceding acid or its ammonium salt with sulphuric acid and subsequently pouring the mass into water, separates from acetic acid in large, dark brown crystals or from benzene in orange-brown needles which melt, after blackening, at 253°; it dissolves slightly in alcohol and to a greater extent in xylene. T. H. P.

[Claisen's Cinnamic Acid Synthesis.] ARTHUR MICHAEL (*Ber.*, 1905, **38**, 4137).—Polemical. A reply to Störmer and Kippe (Abstr., 1905, i, 777). J. J. S.

Synthesis of Tyrosine. PETER W. LATHAM (*Lancet*, 1905, ii, 1757).—A new method of synthesising tyrosine from hydrogen cyanide and *p*-hydroxybenzaldehyde is described. It is pointed out that, in the body, adenine, an isomeride of hydrogen cyanide, may take the place of the latter substance in tyrosine formation. W. D. H.

Synthesis of Amino-acids of Proteid Origin. LOUIS HUGOUNENQ and ALBERT MOREL (*Compt. rend.*, 1906, **142**, 48—49. Compare Abstr., 1905, i, 178, 264, 332).—The symmetrical *p*-hydrocoumaric acid *derivative* of carbamide, $CO[NH\cdot CH(CO_2H)\cdot CH_2\cdot C_6H_4\cdot OH]_2$, precipitated when a slow stream of carbonyl chloride is passed into an aqueous solution of the sodium salt of tyrosine, is very sparingly soluble in water, more soluble in alcohol, from which solution it is precipitated by water in the form of flakes resembling proteid matter. The dry powder darkens at 150°, melts at 240°, and gives a red colour with Millon's reagent. The *p*-hydrocoumaric acid *derivative* of phenylcarbamide, $NHPh\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot C_6H_4\cdot OH$, prepared by the action of phenylcarbimide on the sodium salt of tyrosine, is very sparingly soluble in water, can be crystallised from alcohol, melts and decomposes at 194°, and reacts with Millon's reagent. M. A. W.

Conductivity Measurements with Organic Acids. Josef Hans Süss (*Monatsh.*, 1905, **26**, 1331—1342. Compare Wegscheider, Abstr., 1902, i, 617; and following abstract).—With $\mu_\infty = 375$, nitro-opianic acid has K 0·000291; a week-old solution has a 20 per cent., a solution which has been heated on the water-bath for one hour a 5 per cent., greater conductivity.

5-Nitro-2-aldehydobenzoic acid has K 0·0100 with $\mu_\infty = 378$. 3-Nitro-2-aldehydobenzoic acid has K 0·000130 with $\mu_\infty = 378$. Nitrohemipinic acid $[(CO_2H)_2 : (OMe)_2 : NO_2 = 1:2:3:4:6]$ has K 2·1 with $\mu_\infty = 374$; at the dilution $v = 256$, it shows marked dibasic dissociation, which is not observed with hemipinic acid at the dilution $v = 1000$. The dissociation constant for the second hydrogen atom is $s \times 10^6 =$ 208 or 218.

Aminoterephthalic acid has K 0·0265 with $\mu_\infty = 377$, whilst its 1-methyl ester has K 0·00552 with $\mu_\infty = 376$. Methylaminoterephthalic acid has K 0·030 with $\mu_\infty = 376$. Acetylaminoterephthalic acid has K 0·098 with $\mu_\infty = 375$. A slightly impure specimen of 1-methyl hydrogen acetylaminoterephthalate had K 0·07 with $\mu_\infty =$ 374·4. Acetylmethylaminoterephthalic acid has $K = 0·126$ with $\mu_\infty =$ 374·4.

Homophthalic acid has K 0·0190 with $\mu_\infty = 376·5$; the α-monomethyl ester has K 0·00434 with $\mu_\infty = 375·3$; the β-monomethyl ester has K 0·00764 with $\mu_\infty = 375·3$. The α-monoethyl ester has K 0·0046 with $\mu_\infty = 374·6$; the β-monoethyl ester has K 0·00708 with $\mu_\infty =$ 374·6. 2-Carbamidophenylacetic acid, $NH_2 \cdot CO \cdot C_6H_4 \cdot CH_2 \cdot CO_2H$, has K 0·0050 with $\mu_\infty = 376$. Phenylacetamide-*o*-carboxylic acid,

$$NH_2 \cdot CO \cdot CH_2 \cdot C_6H_4 \cdot CO_2H,$$

has K 0·0089 with $\mu_\infty = 376$.

Phthalonic acid resembles pyruvic acid in that it is a strong acid, the affinity constant of which diminishes rapidly as the dilution increases; it has K 2·14 at the dilution $v = 128$; K 1·91 at $v = 256$; K 1·44 at $v = 512$; and K 1·10 at $v = 1024$. Methyl hydrogen phthalonate, $CO_2Me \cdot CO \cdot C_6H_4 \cdot CO_2H$, prepared by partial hydrolysis of the dimethyl ester, as also by the action of methyl alcohol on the acid, has K 0·015 with $\mu_\infty = 375·7$.

Phenylitaconic acid, $CHPh\colon C(CO_2H) \cdot CH_2 \cdot CO_2H$, has K 0·0137 with $\mu_\infty = 375$; it shows no distinct dibasic dissociation. G. Y.

Constitution of *o*-Aldehydo-acids in Aqueous Solution. Rudolf Wegscheider (*Monatsh.*, 1905, **26**, 1231—1234. Compare Wegscheider, Abstr., 1902, ii, 494; 1903, i, 562).—The affinity constants of *o*-phthalaldehydic, 5-nitro-2-aldehydobenzoic, 3-nitro-2-aldehydobenzoic, and nitro-opianic acids are smaller than those of the corresponding acids without the aldehyde group. These aldehydo-acids must exist in aqueous solution, to a greater or less extent, as the *pseudo*-form,

$C_6H_4 \begin{matrix} \diagup CH(OH) \diagdown \\ \diagdown \; CO \; \diagup \end{matrix} O$, whilst opianic acid, the affinity constant of which is ten times that calculated for the corresponding acid without the aldehyde group, must exist in aqueous solution entirely in the normal or carboxylic form. A comparison of the affinity constants of *o*-phthalaldehydic and opianic acids shows that methoxy-groups in the *ortho*- and *meta*-positions prevent the formation of the *pseudo*-form. The influence of a nitro-group in the *meta*-position to the carboxyl-group on the formation of the *pseudo*-form is only slightly favourable if the nitro- and aldehyde-groups are in the *para*-position, but highly favourable if these groups are in the *ortho*-position to one another. G. Y.

Action of Diazomethane on Aldehydo-acids and Aldehydes.

Hans Meyer (*Monatsh.*, 1905, **26**, 1295—1301. Compare Abstr., 1905, i, 133).—Diazomethane is estimated by shaking its solution with an equal volume of *N*/10 aqueous hydrochloric acid, whereby it is converted into methyl chloride completely in a few seconds, and titrating the excess of acid with *N*/10 alkali hydroxide.

Opianic acid and diazomethane interact energetically to form methyl opianate.

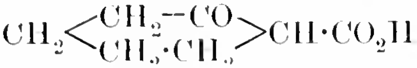
The action of diazomethane on bromo-opianic acid, or of methyl iodide on the silver salt at the laboratory temperature, leads to the formation of *methyl bromo-opianate*, $C_{11}H_9O_5Br$, which crystallises from benzene and melts at 105—106°. The *ψ-methyl* ester, formed by the action of thionyl chloride or of boiling methyl alcohol and sulphuric acid on the acid, crystallises in needles and melts at 109—110°. A mixture of equal amounts of the isomeric esters melts at 70° (compare Bistrzycki and Fink, Abstr., 1898, i, 427).

The action of diazomethane on nitro-opianic acid leads to the formation of the normal ester (Wegscheider, Kušy von Dúbrav, and Rušnov, Abstr., 1904, i, 59).

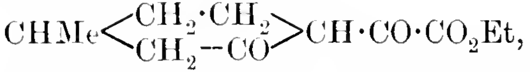
These aldehydo-acids have therefore the normal constitution when anhydrous (compare Wegscheider, preceding abstract), but whilst opianic and bromo-opianic acids give an intense blue coloration with congo-red, and have therefore the normal constitution in aqueous solution, nitro-opianic acid functions in aqueous solution as a *ψ*-acid, as it is entirely without action on the indicator (compare Lobry de Bruyn, Abstr., 1899, i, 861).

Diazomethane does not interact with benzaldehyde or heptoic aldehyde, but evolves nitrogen slowly in contact with the three nitrobenzaldehydes; *o*-nitrobenzaldehyde yields a brown *oil*, which distils apparently without change; *m*-nitrobenzaldehyde yields a *liquid* and a *solid* product; the latter crystallises in colourless needles, melts at 76°, forms an orange-yellow *hydrazone* melting at 127°, on oxidation by permanganate gives *m*-nitrobenzoic acid, but is not identical with *m*-nitroacetophenone, as it is odourless and dissolves in boiling aqueous potassium hydroxide, forming a reddish-yellow solution; *p*-nitrobenzaldehyde yields two *products* melting at 62—65° and at 84° respectively. The more fusible substance, $C_8H_7O_3N$, dissolves in hot aqueous potassium hydroxide to form a rose-coloured solution changing to yellow, and on oxidation yields *p*-nitrobenzoic acid.

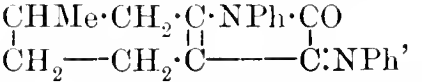
Diazomethane and *p*-chlorobenzaldehyde interact to form a solid *product* which melts at a high temperature. G. Y.

Syntheses by means of the Carboxylic Esters of Cyclic Ketones. Synthesis of Menthone from Methylhexanone. Arthur Kötz and Ludwig Hesse (*Annalen*, 1905, **342**, 306—328).—Since the hydroaromatic β-ketocarboxylic acids, such as *cyclo*hexanone-*o*-carboxylic acid,  $CH_2<\begin{matrix}CH_2\text{--}CO\\CH_2\cdot CH_2\end{matrix}>CH\cdot CO_2H$, would be valuable for synthetical purposes, attempts have been made to prepare such acids with readiness. Endeavours to bring about an internal condensation of esters of dibasic acids in a manner analogous to the formation of ethyl acetoacetate or to condense cyclic ketones with ethyl carbonate led to no result. On the other hand, with ethyl oxalate the ketones yielded ethyl keto-*o*-oxalates.

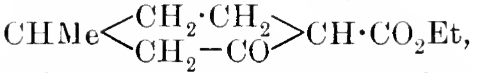
Ethyl 1-*methyl*cyclo*hexane*-3-*one*-4-*oxalate*,



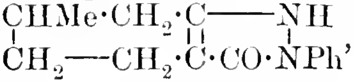
$$CHMe<\begin{matrix}CH_2\cdot CH_2\\CH_2\text{--}CO\end{matrix}>CH\cdot CO\cdot CO_2Et,$$

is prepared from methylhexanone and ethyl oxalate and sodium wire in the presence of light petroleum; the mixture is treated with water and the aqueous solution acidified and extracted with ether, the ketonic ester being finally purified in the form of its copper salt; it is a colourless liquid boiling at 163° under 12 mm. pressure, and has a sp. gr. 1·0903 at 15°. The *copper* salt, $C_{22}H_{30}O_8Cu$, forms crystals melting at 153°; the *semicarbazone* melts at above 245°. 1-*Methyl*cyclo*hexane*-3-*one*-4-*oxalic acid*, prepared from the ester by hydrolysis with 10 per cent. sodium hydroxide, melts and decomposes at 132°. The *semicarbazone* melts at above 245°. When the ester is warmed with aniline, a *compound*,  $\begin{array}{l}CHMe\cdot CH_2\cdot C\cdot NPh\cdot CO\\ \;| \qquad\qquad\quad \| \qquad\qquad |\\ CH_2\text{——}CH_2\cdot C\text{————}C{:}NPh\end{array}$, derived from hexahydroindole, is obtained, crystallising in needles melting at 162·5°.

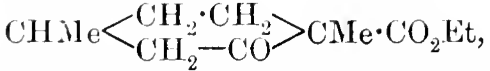
Ethyl 1-*methyl*cyclo*hexane*-3-*one*-4-*carboxylate*,



$$CHMe<\begin{matrix}CH_2\cdot CH_2\\CH_2\text{--}CO\end{matrix}>CH\cdot CO_2Et,$$

prepared by heating the ester just described under reduced pressure at 150—220°, is a colourless oil boiling at 123·5° under 13 mm. and at 165° under 100 mm. pressure, and has a sp. gr. 1·057 at 14°; the *copper* salt is an olive-green powder melting at 155°. With phenylhydrazine, the ester gives a *compound*,  $\begin{array}{l}CHMe\cdot CH_2\cdot C\text{——}NH\\ \;| \qquad\qquad\quad \| \qquad\quad |\\ CH_2\text{——}CH_2\cdot C\cdot CO\cdot NPh\end{array}$, derived from hexahydro-1:2-benzodiazine, which forms crystals melting at 243—245°. With ammonia, the ester yields *ethyl* 3-*amino*-1-*methyl*cyclo*hexane*-4-*carboxylate*,  $CHMe<\begin{matrix}CH_2\text{——}CH_2\\CH_2\cdot C(NH_2)\end{matrix}>C\cdot CO_2Et$, which forms crystals melting at 67°.

Ethyl 1-*dimethyl*cyclo*hexane*-3-*one*-1-*carboxylate*,



$$CHMe<\begin{matrix}CH_2\cdot CH_2\\CH_2\text{--}CO\end{matrix}>CMe\cdot CO_2Et,$$

prepared from ethyl methyl*cyclo*hexanonecarboxylate by treatment with sodium ethoxide and methyl iodide, is an oil boiling at 120—122° under 12 mm. pressure and has a sp. gr. 1·0189 at 19°.

Ethyl 1-*methyl*-4-iso*propyl*cyclo*hexane*-3-*one*-4-*carboxylate*, prepared in analogous manner, is an oil boiling at 135—137° under 10 mm. pressure, and has a sp. gr. 1·009 at 14°. The *semicarbazone* melts at 144—145°. When this ester is hydrolysed by boiling alcoholic potassium hydroxide, menthone is obtained, melting at 206—208°, and feebly dextrorotatory; it yields a semicarbazone melting at 184—185°. K. J. P. O.

Tautomerism. III. Apparent Case of Desmotropy. Paul Rabe and David Spence (*Annalen*, 1905, **342**, 328—355. Compare Abstr., 1901, i, 33, and 1904, i, 749).—The relation between the "acid" and "neutral" forms of Hagemann's ester (Abstr., 1893, i, 393), which the authors (Abstr., 1905, i, 348) have shown to be ethyl 1-methyl-*cyclo*-Δ^6-hexene-5-one-2-carboxylate, has been investigated. The conditions under which the isomerides are prepared do not point to their being tautomeric, and the tautomerism, if it exists, cannot be due to the carbonyl group but rather to the carbethoxyl group. To throw light on these phenomena, ethyl phenylmethyl*cyclo*hexenonecarboxylate, methyl*cyclo*hexenonecarboxylate, and dimethyl*cyclo*hexenonecarboxylate have been prepared. It has been found that two desmotropic isomerides do not exist, but that the esters can be separated into two fractions which show a gradual difference in chemical and physical properties. The cause of these observations will be discussed later.

Ethyl 1-methyl*cyclo*-Δ^6-hexene-5-one-2-carboxylate (*loc. cit.*) boils at 157—159° under 19—21 mm. pressure and has a sp. gr. 1·0775—1·0783 at 20°/4° and a molecular refraction M_{Na} 48·96—49·02. When shaken with 10 per cent. sodium hydroxide at a low temperature, two fractions are obtained; the soluble fraction, the "acid" ester, boils at 160—163° under 24 mm. pressure and has a sp. gr. 1·0701 at 20°/4° and M_{Na} 49·32; an insoluble fraction, the "neutral" ester, boils at 163° under 24 mm. pressure and has a sp. gr. 1·0856 at 20°/4° and M_{Na} 48·27. Both fractions are soluble in concentrated sodium hydroxide, and both give a reaction with ferric chloride. Knoevenagel's ethyl 1:3-dimethyl*cyclo*-Δ^6-hexene-5-one-2-carboxylate behaves in a similar manner; the ethyl 4-hydroxy-2:6-dimethylbenzoate obtained from it by Noyes is readily hydrolysed by alcoholic potassium hydroxide, yielding *4-hydroxy-2:6-dimethylbenzoic acid*, which crystallises in six-sided plates melting and decomposing at 185°.

*Ethyl 1-methyl-3-phenyl*cyclo*-Δ^6-hexene-5-one-2-carboxylate*,

$$CO_2Et\cdot CH\!<\!\begin{matrix}CMe\colon CH_2\\ CPh\cdot CH_2\end{matrix}\!>\!CO,$$

prepared by heating ethyl methylphenyl*cyclo*hexanolonedicarboxylate with sodium ethoxide in alcoholic solution, crystallises in four-sided plates melting at 55°; it dissolves but sparingly in 10 per cent. sodium hydroxide, and only gives a colour with ferric chloride after prolonged boiling. The *semicarbazone* crystallises in needles melting at 158—161°. K. J. P. O.

Preparation of Chloro-derivatives of Indigotin. Badische Anilin- & Soda-Fabrik (D.R.-P. 160817).—When indigotin is chlorinated in absence of water, in the dry state or in indifferent solvents, the chlorine does not enter the nucleus, and only unstable products are obtained. Stable chloro-derivatives of indigotin are obtained, however, when indigotin is suspended in phosphorus oxychloride or sulphuryl chloride, a little iodine being preferably added, and chlorine passed through the well-cooled liquid. The product may be poured on to ice or the volatile compound removed by distillation.

C. H. D.

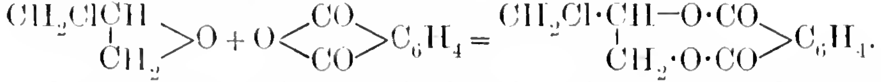
6:6′-Dinitroindigotin. JULIUS SCHWARZ (*Monatsh.*, 1905, **26**, 1253—1263. Compare Baeyer, Abstr., 1879, 937).—5-*Nitrophenylglycine-2-carboxylic acid*, $C_9H_8O_6N_2$, is obtained in a yield of 70 per cent. of the theoretical by boiling five parts of 4-nitro-2-aminobenzoic acid with 10·5 parts of chloroacetic acid and 13·5 parts of sodium carbonate in aqueous solution in a reflux apparatus for eight hours. It crystallises in long, slender, yellow needles, commences to blacken at 225°, melts and decomposes at 240—242°, is readily soluble in alcohol, but only moderately so in acetone, light petroleum, or hot water, yields a reddish-brown, flocculent precipitate, and when heated in a tube sublimes and decomposes partially. The *potassium hydrogen* salt, $C_9H_7O_6N_2K$, crystallises in microscopic, red needles; the *silver* salt, $C_9H_6O_6N_2Ag_2$, is obtained as an orange, voluminous precipitate.

5-*Nitroanildiacetic-2-carboxylic acid*, $C_{10}H_{10}O_8N_2$, is obtained as a by-product in the preparation of 5-nitrophenylglycine-2-carboxylic acid; it crystallises from concentrated hydrochloric acid in long, slender, almost white needles, melts and decomposes at 177°, and forms a *potassium* salt as a yellow precipitate.

1 : 3-*Diacetyl* 6-*nitroindoxyl*,  $NO_2\cdot C_6H_3<\begin{matrix}C(OAc)\\NAc\end{matrix}>CH$, is formed by heating 5-nitrophenylglycine-2-carboxylic acid with sodium acetate and acetic anhydride; it crystallises from alcohol in large, yellow needles, melts at 190°, is almost insoluble in water, but moderately soluble in alcohol, ether, acetone, benzene, or light petroleum, dissolves in warm aqueous sodium carbonate to form a dark green, in concentrated sulphuric acid to form a dark blue, solution, and when warmed with concentrated sulphuric acid yields 6 : 6′-*dinitroindigotin*, $C_{16}H_8O_6N_4$. This is obtained in microscopic, round, dark blue granules, is insoluble in water, almost insoluble in hydrochloric or acetic acids, alcohol, ether, benzene, or light petroleum, is slightly soluble in acetone, and dissolves in hot aniline to form a dark green, in phenol, naphthalene or hot nitrobenzene to form dark blue solutions; when heated in a glass tube, it sublimes, whilst on platinum foil it evolves violet vapours and detonates slightly. On reduction with zinc and hydrochloric acid, it yields 6 : 6′-dinitroindigo-white, and on further reduction 6 : 6′-diaminoindigo-white, which is oxidised by the atmospheric oxygen to 6 : 6′-diaminoindigotin. This is distinguished from 6 : 6′-dinitroindigotin by its solubility in acetic acid, forming a green solution.

G. Y.

Condensation of Epichlorohydrin with Phthalic Anhydride in Presence of Tertiary Bases. ARTHUR WEINSCHENK (*Chem. Zeit.*, 1905, **29**, 1311).—When molecular proportions of epichlorohydrin and phthalic anhydride are warmed together over the water-bath in the presence of a small quantity of dimethylaniline or dimethyltoluidine, the following condensation takes place:

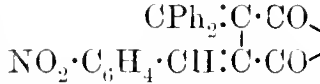


$$\begin{array}{l}CH_2Cl\cdot CH \\ \quad\;\; | \\ \quad\;\; CH_2\end{array}\!\!>O + O<\!\!\begin{array}{l}CO \\ CO\end{array}\!\!>C_6H_4 = \begin{array}{l}CH_2Cl\cdot CH-O\cdot CO \\ \qquad\quad\;\; | \\ \qquad\quad\;\; CH_2\cdot O\cdot CO\end{array}\!\!>C_6H_4.$$

The resulting chloromethylglycol phthalate is a solid below 20°, but between 20° and 30° it assumes a fatty consistency; it is insoluble in water, dissolves with difficulty in alcohol or ether, and is readily soluble in epichlorohydrin. When pyridine is used as the condensing agent, the reaction becomes violent and the mixture rapidly darkens.

P. H.

Butadiene Compounds. XII. Yellow Nitrotriphenylfulgenic Acids and their Red Fulgides. HANS STOBBE and ALBERT KÜLLENBERG (*Ber.*, 1905, **38**, 4081—4087).—*Sodium* α-o-*nitrophenyl-δδ-diphenylfulgenate*, $C_{24}H_{15}O_6NNa_2$, formed by the action of sodium ethoxide on *o*-nitrobenzaldehyde and ethyl γγ-diphenylitaconate in absolute alcoholic solution, crystallises in glistening leaflets from water, or in yellow, monoclinic prisms from 50 per cent. alcohol. The *acid*, $CPh_2{:}C(CO_2H)\cdot C(CO_2H){:}CH\cdot C_6H_4\cdot NO_2,C_2H_6O$, crystallises from alcohol in yellow needles, loses C_2H_6O at 105°, commences to become red at 180°, and melts and evolves gas at 223—224°. The *piperidine* salt, $C_{21}H_{17}O_6N,2C_5H_{11}N$, crystallises in yellow needles and melts and decomposes at 201—202°.

α-o-*Nitrophenyl-δδ-diphenylfulgide*,  $\begin{array}{r}CPh_2{:}C\cdot CO \\ | \;\;\;\;\;\;\; \\ NO_2\cdot C_6H_4\cdot CH{:}C\cdot CO\end{array}\!\!>O$, formed by boiling the acid with acetyl chloride for four hours, is obtained on slow evaporation of the solution in large, pleochroic, monoclinic crystals; it crystallises from a mixture of chloroform and alcohol in blood-red leaflets, from chloroform alone in yellow needles containing chloroform, which is lost gradually on exposure to air, the crystals changing into an orange-red powder; the three modifications melt at 207—208°. Its behaviour towards water, alkali hydroxides, and piperidine is the same as that of dibenzylidenesuccinic anhydride (Stobbe, Naoúm, and Kautzsch, Abstr., 1904, i, 589); when oxidised, it yields benzophenone and *o*-nitrobenzoic acid.

α-m-*Nitrophenyl-δδ-diphenylfulgenic acid* is obtained in the form of its *sodium* salt, $C_{24}H_{15}O_6NNa_2$, by digesting *m*-nitrobenzaldehyde and ethyl γγ-diphenylitaconate with sodium ethoxide in absolute alcoholic solution; this crystallises in yellow leaflets. The *acid*, $C_{21}H_{17}O_6N$, crystallises in white leaflets or prisms from ether, in yellow leaflets from acetic acid, and melts and decomposes at 221—222°. The *piperidine* salt, $C_{24}H_{17}O_6N,2C_5H_{11}N$, forms yellow needles and melts and decomposes at 177—178°.

α-m-*Nitrophenyl-δδ-diphenylfulgide*, $C_{24}H_{15}O_5N$, crystallises from a mixture of chloroform and alcohol in orange-red, slender needles, or from benzene in stellate groups of pleochroic, monoclinic prisms, and melts at 194—195°.

α-p-*Nitrophenyl-δδ-diphenylfulgenic acid*, $C_{24}H_{17}O_6N$, from *p*-nitrobenzaldehyde and ethyl γγ-diphenylitaconate, crystallises in yellow prisms, melts and decomposes at 238°, and when oxidised yields benzophenone, *p*-nitrobenzaldehyde, and *p*-nitrobenzoic acid. The *sodium* salt crystallises in yellow prisms; the *piperidine* salt forms nodular aggregates of slender, yellow needles and melts and decomposes at 181—182°.

α-p-*Nitrophenyl-δδ-diphenylfulgide*, $C_{21}H_{15}O_5N$, crystallises in orange, pleochroic, monoclinic plates melting at 228°, or from a mixture of benzene and chloroform in similar crystals melting at 224°. G. Y.

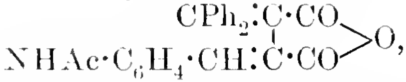
Butadiene Compounds. XIII. Aminotriphenylfulgenic Acid. Hans Stobbe and Albert Küllenberg (*Ber.*, 1905, **38**, 4087—4090).—The α-aminophenyl-δδ-diphenylfulgenic acids are formed by reducing the corresponding α-nitrophenyl acids with ferrous sulphate in ammoniacal solution and precipitating the product with the calculated quantity of *N*-hydrochloric acid.

α-o-*Aminophenyl-δδ-diphenylfulgenic acid*,

$$CPh_2{:}C(CO_2H){\cdot}C(CO_2H){:}CH{\cdot}C_6H_4{\cdot}NH_2,$$

is obtained as a yellow, amorphous mass, which melts and decomposes at 175—177° and is readily soluble in hydrochloric acid. The *piperidine* salt, $C_{24}H_{19}O_4N,2C_5H_{11}N$, crystallises in yellow needles, melts and decomposes at 192—193°, and on treatment with aqueous silver nitrate forms the *silver* salt, $C_{24}H_{17}O_4NAg_2$, as a white, flocculent precipitate which becomes yellow on drying.

α-m-*Aminophenyl-δδ-diphenylfulgenic acid*, $C_{24}H_{19}O_4N$, crystallises in yellow, monoclinic prisms, melts and decomposes at 224°, and when boiled with acetyl chloride forms α-m *acetylaminophenyl-δδ-diphenylfulgide*,



$$\begin{array}{l}CPh_2{:}C{\cdot}CO\\ NHAc{\cdot}C_6H_4{\cdot}CH{:}C{\cdot}CO\end{array}\!\!>O,$$

which crystallises in slender, yellow needles and melts at 215°. The *piperidine* salt,

$$C_{24}H_{19}O_4N,2C_5H_{11}N,$$

forms long, dirty-yellow needles and melts and decomposes at 177—178°.

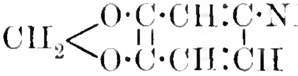
α-p-*Aminophenyl-δδ-diphenylfulgenic acid* is amorphous; the *piperidine* salt forms large, dark yellow crystals and melts and decomposes at 182—183°; the *copper* salt, $C_{27}H_{17}O_4NCu$, is obtained as a light brown, amorphous precipitate. G. Y.

Resin Acids from Conifers. V. Albert Vesterberg (*Ber.*, 1905, **38**, 4125—4132. Compare Abstr., 1886, 365, 1038; 1888, 294; 1904, i, 151; Ducommun, *Chem. Zeit.*, 1885, 1592).—Although *d*- and *l*-pimaric acids yield sparingly soluble, crystalline ammonium salts, a mixture of either acid with a large quantity of abietic acid produces a gelatinous salt. When the two acids are in the proportions 1 : 10, the salt remains gelatinous for weeks, but in the proportions 1 : 5 crystals are often observed in the course of a few days.

The separation of the pimaric acid is best accomplished by the following processes: (*a*) fractional crystallisation of the acids from 85 per cent. (vol.) alcohol until an acid is obtained which gives a crystalline ammonium salt; (*b*) repeated crystallisation of the sodium salt from water containing a small amount of sodium hydroxide; (*c*) crystallisation of the acid from alcohol or acetic acid.

d-Pimaric acid has been isolated by this method from French colophony and from the resin of *Pinus sylvestris*. J. J. S.

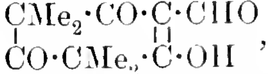
Positions of the NO_2 and NH_2 Groups in the Mononitro- and Amino-derivatives of Piperonylaldehyde and Piperonylic Acid. Efisio Mameli (*Atti R. Accad. Lincei*, 1905, [v], 14, ii, 424—432, 510—518).—The positions of the substituent nitrogen chains in the nitro- and amino-derivatives of piperonaldehyde and of the corresponding acid have not yet been absolutely proved (compare Abstr., 1904, i, 668, 743, and 1023; 1905, i, 203, 889). The following are the results of the author's investigations on this subject.

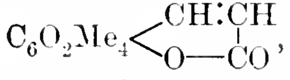
The oxidation of nitropiperonaldehyde yields the nitropiperonylic acid melting at 172° and already obtained by Jobst and Hesse by the nitration of piperonylic acid (Abstr., 1878, 733; 1880, 325). This nitro-acid or its calcium salt, when decomposed by heat, yields nitrocatechol methylene ether, which can also be obtained by distilling an alkaline solution of nitropiperonaldehyde in a current of steam. The nitro-groups in nitropiperonaldehyde and in nitrocatecholmethylene ether must have the same position relatively to the other substituents as that in nitropiperonylic acid. Reduction of the last-named compound gives rise to the *p*-aminocatechol methylene ether (6-amino-3 : 4-methylenecatechol),  $CH_2<\begin{matrix}O\cdot C\cdot CH:C\cdot NH_2\\ O\cdot C\cdot CH:CH\end{matrix}$, already prepared by Rupe and von Majewski (Abstr., 1901, i, 103), by van Linge (Abstr., 1897, i, 618), and by Hesse (*loc. cit.*). The nitro-group in nitropiperonylic acid must therefore occupy the 6-position with reference to the carboxyl group, the $-O\cdot CH_2\cdot O-$ group being in the 3 : 4-position. Confirmation of this conclusion has been obtained by preparing, from nitropiperonylaldehyde and from nitropiperonylic acid, the 4-nitro-1 : 2-dihydroxybenzene described by various authors.

The results given indicate that, when piperonaldehyde or piperonylic acid is nitrated directly, the first nitro-group introduced enters in the 6-position with respect to the aldehyde or carboxyl group in position 1, and the dioxymethylene complex in the position 3 : 4, and that further nitration gives rise to symmetrical tetra-substituted derivatives.

The above constitution for nitropiperonaldehyde has been confirmed in an indirect manner by the recent work of Herz (Abstr., 1905, i, 778). T. H. P.

Tetramethylphloroglucinolaldehyde. Josef Herzig and Franz Wenzel (*Monatsh.*, 1905, 26, 1359—1389. Compare Abstr., 1904, i, 251).—[With Peter Rona.]—Dimethylphloroglucinolaldehyde is heated with methyl iodide and potassium hydroxide in methyl-alcoholic solution in a reflux apparatus during one day, and after addition of further quantities of potassium hydroxide and methyl iodide again for one day. After distillation of the alcohol, the residue is treated with water and ether, when there are obtained an aqueous solution of the potassium derivative of tetramethylphloroglucinolaldehyde (1) and an ethereal solution of a condensation product (2).

(1) *Tetramethylphloroglucinolaldehyde*,  $\begin{matrix}CMe_2\cdot CO\cdot C\cdot CHO\\ CO\cdot CMe_2\cdot C\cdot OH\end{matrix}$, obtained on acidification of the alkaline solution, crystallises from ether in large prisms or from methyl alcohol in colourless, rectangular plates, melts

at 70—71°, is readily soluble in benzene, but less soluble in methyl or ethyl alcohol, and dissolves in aqueous potassium hydroxide to form a colourless solution which remains unchanged on prolonged warming; it may be titrated with $N/10$ potassium hydroxide, using phenolphthalein as indicator. The *potassium* derivative, $OK\cdot C_6O_2Me_4\cdot COH$, forms colourless crystals and is not decomposed by carbon dioxide in aqueous solution. The *oxime*, $OH\cdot C_6O_2Me_4\cdot CH\colon NOH$, crystallises from ethyl acetate in white needles, commences to decompose at 189°, and melts at 196° to a dark yellow mass. When heated with acetic anhydride and sodium acetate at 160—180°, or when boiled with acetic anhydride only, tetramethylphloroglucinolaldehyde forms the *coumarin* derivative,  $C_6O_2Me_4\Big<\begin{array}{l}CH\colon CH\\ \quad\ \ |\\ O—CO\end{array}$, which crystallises from methyl alcohol and melts at 205—208°. The *methyl ether*, $OMe\cdot C_6O_2Me_4\cdot CHO$, is formed by the action of diazomethane on tetramethylphloroglucinolaldehyde in ethereal solution; it crystallises from alcohol and melts at 100°. When oxidised with potassium permanganate in alkaline solution, the aldehyde yields a *substance* which crystallises in glistening scales, melts and evolves gas at 100°, and when heated with alcohol or benzene forms carbon dioxide and the condensation product melting at 210—212°.

[With WILHELM REISMANN.]—(2) The *condensation product* (6-*hydroxy*-2:2':4:4':6'-*pentaketo*-3:3:3':3':5:5:5':5'-*octamethyltetrahydrophenylphenylidenemethane*),

$$CO\Big<\begin{array}{l}CMe_2\cdot C(OH)\\ CMe_2——CO\end{array}\Big>C\cdot CH\colon C\Big<\begin{array}{l}CO\cdot CMe_2\\ CO\cdot CMe_2\end{array}\Big>CO,$$

is obtained on evaporation of the ethereal solution and treatment of the residue with benzene; it is formed also together with formic acid when tetramethylphloroglucinolaldehyde is dissolved in dilute methyl alcohol, or is boiled with water, or when its potassium derivative is treated with methyl sulphate. After repeated recrystallisation from a mixture of chloroform and light petroleum, it forms nodular aggregates of white needles and melts at 217°; it does not yield an acetyl derivative when boiled with sodium acetate and acetic anhydride. The *methyl ether*, $C_{21}H_{25}O_5\cdot OMe$, formed by the action of diazomethane on the condensation product in ethereal solution, separates from alcohol in colourless crystals, melts at 163—164°, and when treated with hydroxylamine hydrochloride in presence of sodium hydrogen carbonate or sodium methoxide yields a *product* which contains nitrogen and melts at 182°.

The condensation product dissolves in aqueous potassium hydroxide to form a yellow solution which becomes colourless, slowly at the laboratory temperature, quickly on evaporation, with formation of the potassium derivative of tetramethylphloroglucinolaldehyde and tetramethylphloroglucinol, melting at 192° (m. p. 187—188°; Reisch, Abstr., 1899, i, 803). The condensation product is again formed when the products of its hydrolysis are boiled with water containing a few drops of hydrochloric acid.

The action of methyl-alcoholic potash on the methyl ether of the condensation product leads to the hydrolysis of the methoxy-group, and therefore to the formation of the same decomposition products as are obtained from the hydroxy-compound. When treated with concentrated sulphuric acid, the methyl ether yields the condensation product.

When reduced with zinc dust and aqueous potassium hydroxide, the condensation product forms a *dihydro*-derivative, $C_{21}H_{28}O_6$, which crystallises from benzene in slender needles and melts at 173°. It is formed also from tetramethylphloroglucinol by the action of (*a*) formaldehyde and concentrated sulphuric acid at 40°; (*b*) of formaldehyde and potassium hydroxide in warm methyl-alcoholic solution; or (*c*) of boiling aqueous formaldehyde. The *methyl ether*, $C_{21}H_{26}O_4(OMe)_2$, formed by the action of diazomethane on the reduction product in ethereal solution, crystallises from methyl alcohol in stout needles, melts at 81°, and when boiled with hydriodic acid forms an *anhydride*, $C_{21}H_{26}O_5$, which is formed also by the action of concentrated sulphuric acid on the reduction product on the water-bath, or by boiling this with acetic anhydride and sodium acetate; it crystallises in needles and melts at 190°.

On prolonged action of potassium hydroxide and methyl iodide on dimethylphloroglucinolaldehyde, there is formed, in addition to tetramethylphloroglucinolaldehyde and its condensation product, a substance, $C_{22}H_{26}O_5$, which crystallises in glistening needles and melts at 173°. G. Y.

Hydroxylamine Derivatives of Ketones of the Type $CO(CH{:}CHR)_2$.

Gaetano Minunni and Riccardo Ciusa (*Atti R. Accad. Lincei*, 1905, [v], **14**, ii, 420—424. Compare Abstr., 1905, i, 245).—Attempts to determine the constitution of the base $C_{17}H_{18}N_2$, obtained by reducing α-dibenzylideneacetonehydroxylamineoxime (*loc. cit.*), by preparing its oxidation products have been unsuccessful. The compound, $C_{17}H_{16}N_2(OH)_2$, prepared by reducing disalicylideneacetonehydroxylamineoxime, gives mainly resinous products on oxidation, only a small quantity of a crystalline product being obtained by treatment with potassium permanganate and sulphuric acid.

Bromo-α-dibenzylideneacetonehydroxylamineoxime, $C_{17}H_{18}O_2N_2Br$, separates from alcohol in white crystals melting and decomposing at 172° and dissolves in methyl alcohol or chloroform and, to a slight extent, in ethyl acetate.

Oxidation of α-dibenzylideneacetonehydroxylamineoxime by means of amyl nitrite or acid potassium permanganate solution yields a small quantity of a *substance*, $C_{17}H_{14}ON_2$, separating from aqueous alcohol in yellow crystals which soften at 165°, melt and decompose at 176°, and are soluble in almost all the organic solvents.

Reduction of β-dibenzylideneacetonehydroxylamineoxime by means of sodium in amyl alcohol solution, gives an oily base, the hydrochloride of which melts at 234° and the platinichloride at 268°; the *benzoyl* derivative, $C_{17}H_{17}N_2Bz$, of the base crystallises from a mixture of ethyl acetate and alcohol in white needles which blacken at 260°, melt at 290°, and dissolve readily in methyl or ethyl alcohol and, to a less extent, in carbon tetrachloride.

Disalicylideneacetonehydroxylamineoxime, $C_{17}H_{16}O_2N_2(OH)_2$, crystal-

lises from alcohol in hard prisms melting and decomposing at 207°, and is slightly soluble in ether, benzene, ethyl acetate, or methyl alcohol; it dissolves in potassium hydroxide solution or in hydrochloric acid, and also in sulphuric acid, to which it imparts a blood-red coloration. Its *tetrabenzoyl* derivative, $C_{17}H_{14}O_4N_2Bz_4$, crystallises from alcohol in hard, minute prisms melting at 135°, and dissolves readily in methyl alcohol and, to a slight extent, in ether, benzene, or ethyl acetate. On reduction with sodium and amyl alcohol, it gives a *compound*, $C_{17}H_{16}N_2(OH)_2$, which crystallises from alcohol in white leaflets melting and decomposing at 191° and is soluble in ether or benzene with difficulty, in ethyl acetate with greater readiness, and in acetic, hydrochloric, or sulphuric acid or potassium hydroxide solution very readily.
T. H. P.

Reaction between Organic Magnesium Compounds and Unsaturated Compounds. VII. Complex Products from Cinnamic Esters.

Elmer P. Kohler and Gertrude Heritage (*Amer. Chem. J.*, 1905, **34**, 568—580).—*Phenyl α-phenylcinnamate* crystallises in needles, melts at 142°, is sparingly soluble in alcohol or ether, moderately so in acetone or benzene, and readily in chloroform. When a solution of the ester in benzene is boiled with excess of magnesium phenyl bromide, *triphenylpropiophenone*,

$$CHPh_2{\cdot}CHPh{\cdot}COPh,$$

is produced, which crystallises in small, colourless needles, melts at 182°, is readily soluble in chloroform, moderately so in benzene or hot acetone, and very slightly in alcohol or ether; it yields neither a hydrazone nor an oxime.

When phenyl cinnamate (1 mol.) is added to a well-cooled ethereal solution of magnesium phenyl bromide (3 mols.) and the product is decomposed with cold hydrochloric acid, diphenylpropionic acid and diphenylpropiophenone are produced together with a small quantity of diphenyl. If the solution of the bromide (1 mol.) is slowly added to a cold solution of the ester (1 mol.), a *substance*,

$$CHPh_2{\cdot}CH(CO_2Ph){\cdot}CO{\cdot}CH_2{\cdot}CHPh_2,$$

is produced which crystallises in long needles, melts at 180—182°, is readily soluble in chloroform or benzene, moderately in ethyl acetate or hot acetone, and very slightly in alcohol or ether; it is easily hydrolysed by potassium hydroxide with formation of potassium phenoxide, potassium carbonate, and *ααεε-tetraphenylpentane-γ-one*, $CO(CH_2{\cdot}CHPh_2)_2$, which crystallises in colourless needles, melts at 130°, is readily soluble in ethyl acetate or chloroform, and moderately so in alcohol or acetone, does not combine with bromine, and is not attacked by potassium permanganate. Tetraphenylpentanone *oxime* crystallises in needles, melts at 115—116°, and when treated with phosphorus pentachloride is converted into the isomeric *acid anilide*, which forms small, lustrous prisms, melts at 155°, and if heated in a sealed tube with strong hydrochloric acid yields ββ-diphenylpropionic acid and ββ-diphenylethylamine.

In an earlier paper (Abstr., 1905, i, 208), the effect of adding methyl cinnamate to an excess of magnesium phenyl bromide was described.

If, on the other hand, the magnesium compound is added slowly to a well-cooled solution of methyl cinnamate, a *methyl* ester,

$$CHPh_2\cdot CH(CO_2Me)\cdot CO\cdot CH_2\cdot CHPh_2,$$

corresponding with the phenyl ester obtained from phenyl cinnamate under the same conditions, is produced, which crystallises in slender needles, melts at 211—213°, is readily soluble in chloroform or benzene, moderately in acetone, and very slightly so in alcohol or ether; when heated at 200° with concentrated hydrochloric acid, it is decomposed with formation of 2 mols. of $\beta\beta$-diphenylpropionic acid. *β-Benzoyl-ααεε-tetraphenylpentane-γ-one*, $CHPh_2\cdot CHBz\cdot CO\cdot CH_2\cdot CHPh_2$, which is obtained as a by-product in the preparation of the methyl ester just described, and can be prepared by dropping methyl cinnamate into a boiling solution of magnesium phenyl bromide, crystallises in needles, melts at 166°, is readily soluble in chloroform or acetone, moderately in alcohol, and sparingly so in ether. This ketone is hydrolysed by boiling alcoholic potassium hydroxide with formation of tetraphenylpentanone and potassium benzoate, whilst aqueous potassium hydroxide converts it into diphenylpropiophenone and potassium diphenylpropionate. If ethereal solutions of methyl cinnamate and magnesium phenyl bromide are boiled together for three or four hours and the product is treated with ice-water, a crystalline *substance*,

$$CHPh_2\cdot CH(CPh_2\cdot OH)\cdot CO\cdot CH_2\cdot CHPh_2,$$

is obtained, which melts at 153°, is readily soluble in acetone or chloroform, and moderately so in alcohol, and when heated alone at 270—300°, or with concentrated hydrochloric acid at 200°, is converted into benzophenone and tetraphenylpentanone. E. G.

Soluble Preparations of *o*-Nitrophenyl-β-lactomethylketone. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 160783).—*o*-Nitrophenyl-β-lactomethylketone is useful for the production of indigo-blue on the fibre, but is very sparingly soluble. It dissolves, however, in aqueous solutions of the alkali salts of benzylanilinesulphonic acid, $CH_2Ph\cdot NH\cdot C_6H_4\cdot SO_3H$, 2 mols. of the ketone requiring at least 1 mol. of the acid for solution. Salts of benzyltoluidinesulphonic acids or of chlorobenzylanilinesulphonic acids, and homologues of the ketone, show a similar behaviour. C. H. D.

Derivatives of Tetrachloro-*o*-benzoquinone. C. LORING JACKSON and R. D. MAC LAURIN (*Ber.*, 1905, 38, 4103—4105).—*Hexachloro-o-quinocatechol ether*, $C_6O_2Cl_2{<}\substack{O\\O}{>}C_6Cl_4$, prepared by the action of tetrachlorocatechol on tetrachloro-*o*-benzoquinone dissolved in dilute acetic acid, separates from benzene in deep red crystals, melts at 300°, and is more soluble than the bromo-compound (Jackson and Koch, Abstr., 1901, i, 597). It is reduced by sodium amalgam to *hexachlorodihydroxycatechol ether*, $C_6Cl_2(OH)_2{<}\substack{O\\O}{>}C_6Cl_4$, which crystallises from alcohol in colourless needles and melts at 290°. When condensed with aniline, tetrachloro-*o*-benzoquinone yields a double compound, *aniline-dichlorodianilino-o-benzoquinone*,

$$C_6O_2Cl_2(NHPh)_2,NH_2Ph,$$

which crystallises from benzene in long, thin, brown needles and melts and decomposes at 164—165°. The *alcohol* compound,

$$C_6O_2Cl_2(NHPh)_2,C_2H_6O,$$

crystallises from alcohol in glistening, yellow plates and melts at 140—141°. *Dichlorodianilino* o-*benzoquinone*, $C_6O_2Cl_2(NHPh)_2$, prepared by crystallising the aniline compound from a mixture of benzene and light petroleum, separates in reddish-purple, pointed needles and melts at 194—195°. *Chlorodianilino*-p-*quinoneanil*,

$$O:C_6HCl(NHPh)_2:NPh,$$

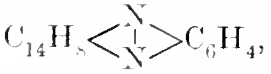
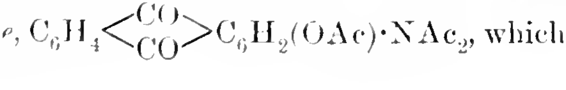
prepared by the action of alcohol and aniline on the preceding compound, crystallises from benzene and alcohol in broad, black, glistening needles and melts at 180°. T. M. L.

1 : 2-Anthraquinone. Kasimir Lagodzinski (*Annalen*, 1905, **342**, 59—89. Compare Abstr., 1904, i, 158).—1-*Nitroso-2-anthrol*, which the author regards as being in the tautomeric form, $O:C_{14}H_8:N\cdot OH$, can be prepared from 2-anthrol in alcoholic solution by treatment, successively, with an aqueous solution of zinc chloride and sodium nitrite; the mixture is slowly heated and the zinc salt of the nitrosoanthrol separates; it crystallises in orange needles decomposing at 188°, and gives an indigo-blue coloration with concentrated sulphuric acid. The *potassium* derivative, $C_{14}H_8O_2NK$, forms green and the *sodium* derivative yellowish-green leaflets. The *ethyl ether*,

$$O:C_{14}H_8:N\cdot OEt,$$

prepared from the silver salt and ethyl iodide, crystallises in golden-yellow leaflets melting at 143°. The *methyl ether* crystallises in similar forms, melting at 129—130°.

1-*Amino-2-anthrol*, $NH_2\cdot C_{14}H_8\cdot OH$, is obtained by reducing either the nitrosoanthrol with stannous chloride and hydrochloric acid or with hydrogen sulphide in alkaline solution, or benzeneazo-2-anthrol with zinc dust and hydrochloric acid; it crystallises in yellowish-green leaflets decomposing at 140—150°; the *hydrochloride* and the *sulphate* form greenish-yellow needles; when heated with concentrated sulphuric acid, a blood-red coloration is obtained. A *triacetyl* derivative, $NAc_2\cdot C_{14}H_8\cdot OAc$, crystallises in greenish-grey leaflets melting at 165°, and dissolves in alcohol solution with a blue fluorescence; on hydrolysis with dilute alcoholic potassium hydroxide, 1-*acetylamino* 2-*anthrol* is obtained as green leaflets decomposing at 200—220°; its alcoholic solution has a bluish-green fluorescence.

1 : 2-*Anthraquinone*, $C_{14}H_8O_2$, is formed when the salts of aminoanthrol are oxidised in the cold with ferric chloride or chromic acid; it crystallises in orange-yellow needles melting and decomposing at 185—190°, and dissolves in sulphuric acid with a bluish-violet coloration. It condenses with *o*-phenylenediamine, yielding 1 : 2-*anthraphenazine*,  $C_{14}H_8<\overset{N}{\underset{N}{|}}>C_6H_4$, which crystallises in dark yellow leaflets melting at 221—222°; the *hydrochloride* is cherry-red and the *sulphate* bluish-green. When oxidised with chromic acid in acetic acid solution, triacetylaminoanthrol yields 1-*diacetylamino-2-acetoxyanthraquinone*,  $C_6H_4<\overset{CO}{\underset{CO}{}}>C_6H_2(OAc)\cdot NAc_2$, which crystallises in pale

yellow needles melting at 189°. On hydrolysis, it is converted into 1-*amino-2-hydroxyanthraquinone*, crystallising in dark red needles melting at 250—251° and identical with Liebermann's α-alizarinamide. Alizarin is produced by heating the substance last mentioned under pressure with hydrochloric acid at 250°; the transformation is not produced by diazotisation.

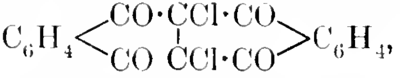
1 : 2-Anthraquinol (*loc. cit.*), prepared from the quinone, crystallises in greenish-yellow leaflets melting and decomposing at 131°; the alkaline solution is at first cherry-red, but soon blackens on oxidation. The *diacetyl* derivative forms yellow aggregates melting at 145°, and by oxidation with chromic acid is converted into diacetylalizarin.

K. J. P. O.

Chlorination of Mono- and Di-amino-derivatives of Anthraquinone. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 158951. Compare Wohl, this vol., i, 9).—The mono- and di-amino-derivatives of anthraquinone are readily chlorinated by means of sulphuryl chloride. Thus, β-aminoanthraquinone yields a monochloro-derivative, 1 : 5-diaminoanthraquinone yields a tetrachloro-derivative, crystallising from nitrobenzene in glistening, brown needles, and 2 : 6-diaminoanthraquinone yields a dichloro-derivative. The solubilities of many such chloro-compounds in sulphuric acid and in organic solvents are described.

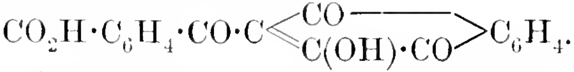
C. H. D.

Studies in the Naphthacene Series. HUGO VOSWINCKEL (*Ber.*, 1905, **38**, 4015—4021).—Naphthacenediquinone (Gabriel and Leupold, Abstr., 1898, i, 482) dissolved in glacial acetic acid is attacked by chlorine at the ordinary temperature, giving the *dichloride*,



$$C_6H_4<\begin{matrix}CO\cdot CCl\cdot CO\\ CO\quad CCl\cdot CO\end{matrix}>C_6H_4,$$

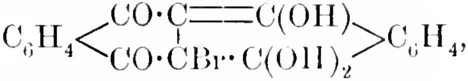
which crystallises from nitrobenzene in rhombic crystals and melts at 175°; with reducing agents it gives dihydroxynaphthacenequinone (Gabriel and Leupold, *loc. cit.*), and on warming with dilute aqueous sodium hydroxide the same substance is also formed, but the principal product is an *acid*, $C_{18}H_{10}O_6$, perhaps



$$CO_2H\cdot C_6H_4\cdot CO\cdot C<\begin{matrix}CO\text{———}\\ C(OH)\cdot CO\end{matrix}>C_6H_4.$$

This crystallises from dilute alcohol containing hydrochloric acid in bright yellow, transparent prisms, melts at 185°, and gives a hydrazone and a red, crystalline *silver* salt, $C_{18}H_8O_6Ag_2,H_2O$.

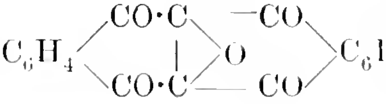
With bromine in glacial acetic acid, naphthacenediquinone gives *trihydroxynaphthacenequinone bromide*,



$$C_6H_4<\begin{matrix}CO\cdot C{=\!=}C(OH)\\ CO\cdot CBr\cdot C(OH)_2\end{matrix}>C_6H_4,$$

which separates in well-formed, colourless prisms and melts at 198°; a little dihydroxynaphthacenequinone is also formed. When the bromide is shaken with aqueous sodium hydroxide, it seems to yield the acid, $C_{18}H_{10}O_6$, described above, but the melting point is slightly higher, namely, 199°.

Naphthacenediquinone oxide,



$$C_6H_4<\begin{matrix}CO\cdot C\text{—}CO\\ \quad | \;\; >O\\ CO\cdot C\text{—}CO\end{matrix}>C_6H_4,$$

prepared

by leaving powdered naphthacenediquinone with an aqueous suspension of bleaching powder for several days, crystallises from benzene in small, orange-coloured needles, melts and decomposes at about 240°, and is easily reduced to dihydroxynaphthacenequinone; with aqueous sodium hydroxide, the acid, $C_{18}H_{10}O_6$, is obtained, melting at 199°.

W. A. D.

Preparation of Bornylenediamine. Paul Duden (D.R.-P. 160103).—Bornylenediamine (camphanediamine) is prepared by reducing amino-, *iso*nitroso-, or *iso*nitro-camphoroxime by means of sodium and alcohol, sodium amalgam, or electrolytic hydrogen. *Bornylenediamine* forms a waxy solid, boils at 246°, and dissolves with extreme readiness in water. The *diacetyl* derivative occurs in two stereoisomeric modifications, melting at 246° and 253° respectively.

C. H. D.

Chemical Investigation of Resin from the Pine (*Pinus abies*). Peter Klason and John Köhler (*Arkiv Kem. Min. Geol.*, 1905, **2**, i, No. 3, 1—39).—Resin from the pine contains two isomorphous acids, *a*- and *β*-colophonic acids, $C_{20}H_{30}O_2$. The acids have the normal molecular weight in freezing acetic acid and give the acid value 185·4. The separate acids have not been obtained absolutely pure, so that the physical constants given below are only approximately correct.

a-Colophonic acid crystallises from alcohol in colourless, oblique, monoclinic prisms [$a:b:c = 1·1282:1:0·9716$; $\beta = 71°24'$], melts at 177—182°, and has $[a]_D - 59·41°$.

β-Colophonic acid separates in less well-developed crystals than the *a*-acid, melts at 168—173°, and has $[a]_D + 52·2°$.

The *ammonium*, $NH_3,2C_{20}H_{30}O_2$, *calcium*, $Ca(C_{20}H_{29}O_2)_2$, and *barium*, $Ba(C_{20}H_{29}O_2)_2,2H_2O$, salts of the mixed acids were prepared.

T. H. P.

Gutta Percha and Balata. William A. Caspari (*J. Soc. Chem. Ind.*, 1905, **24**, 1274—1278).—Analyses of various guttas and balata, purified by solution in benzene and precipitation with alcohol thrice repeated, confirmed the formula $(C_5H_8)_n$. Pure gutta is of a leathery consistence and almost destitute of elasticity; below 100°, it becomes soft and can be kneaded, whilst caoutchouc becomes sticky and moderately plastic, but retains some resilience; at higher temperatures, the two hydrocarbons tend to approximate in behaviour. When dissolved in dry carbon tetrachloride and treated with chlorine, the hydrocarbons of gutta, caoutchouc, or balata yielded substances the composition of which approximated to the formula $C_{20}H_{36}Cl_{14}$; the substances, when purified by precipitation from dilute benzene or chloroform solution by means of alcohol and dried in a vacuum, presented white, toughish plates. Substances prepared similarly by the action of bromine gave analytical numbers leading to the formula $C_{30}H_{46}Br_{10}$; iodine in chloroform solution yielded substances containing between 12·11 and 13·47 per cent. of iodine. Benzene solutions of gutta or balata saturated with dry hydrogen chloride and precipitated with alcohol gave substances which, when redissolved and again precipitated, formed white, leathery flakes, easily soluble in benzene or in chloroform, and had the composition $C_{30}H_{45},5HCl$; the behaviour of caoutchouc was found to be somewhat different. A solution of nitrogen peroxide and oxygen in benzene, added to a benzene solution of the hydrocarbons, produced green, gelatinous precipitates of variable composition; on adding more nitrogen peroxide, yellow clots separated, which had the composition $C_{10}H_{16}O_4N_2$; on subjecting these substances to the protracted action of nitrogen peroxide, they produced substances which, when pure, were saffron-yellow powders which dissolved in acetone, ethyl acetate, alkalis, and ammonia with a deep orange colour; their composition is represented by the formula $C_{10}H_{15}O_7N_3$. By the action of nitric acid, a substance of the formula $C_{15}H_{21}O_{11}N_4$ was obtained. Benzene solutions of the hydrocarbons on treatment with dry nitric oxide gave substances the composition of which is represented by the formula $C_{10}H_{16}O_2N$. The conclusion is drawn from these experiments that the hydrocarbons of gutta percha and of balata are identical, whilst as regards gutta and caoutchoucs it seems as if these were a common molecule, differences in the aggregation of which caused differences in mechanical structure.

P. H.

Butadiene Compounds. XI. Parallel Coloured Furyl- and Phenyl-fulgides. HANS STOBBE and RICHARD ECKERT (*Ber.*, 1905, **38**, 4075—4081).—The furyl group has stronger chromophoric properties than has the phenyl group; a number of furyl and the corresponding phenyl compounds are quoted to show that where these have the same colour, the former have the deeper shade. This is the case in the fulgide series, the three furyl-fulgides described below being light orange, dichromate-red, and reddish-brown, whilst the corresponding phenyl compounds are light yellow, orange-red, and lemon-yellow respectively (Abstr., 1905, i, 857; this vol., i, 22).

a-Furyl-δδ-dimethylfulgenic (*a-furfurylideneteraconic*) *acid*,

$$CMe_2{:}C(CO_2H){\cdot}C(CO_2H){:}CH{\cdot}C_4OH_3,$$

formed by the action of sodium ethoxide on ethyl dimethylitaconate and furfuraldehyde in absolute alcoholic solution, separates from 20 per cent. acetic acid in small, slightly yellow, rhombic crystals, softens at 204°, and melts and decomposes at 218°. When treated with acetyl chloride, cooled by a freezing mixture, it yields *a-furyl-δδ-dimethylfulgide*, $C_{12}H_{10}O_4$, which crystallises from light petroleum in small, light orange, monoclinic prisms, melts at 63°, is readily soluble in ether, chloroform, benzene, or carbon disulphide, and dissolves in concentrated sulphuric acid to form a yellow solution, which becomes greenish-brown, and finally reddish-brown, changing to yellow on dilution with water.

δδ-Diphenyl-a-furylfulgenic acid,

$$CPh_2{:}C(CO_2H){\cdot}C(CO_2H){:}CH{\cdot}C_4OH_3,$$

formed from furfuraldehyde and ethyl diphenylitaconate in alcoholic sodium ethoxide solution, crystallises from benzene in shimmering, yellow leaflets containing C_6H_6, which is lost at 100°, becomes dark at 187°, and melts and decomposes at 202°. The *sodium* salt,

$C_{22}H_{14}O_5Na,2H_2O,2C_2H_6O$, crystallises from 70 per cent. alcohol in white plates.

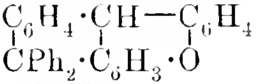
δδ-*Diphenyl-α-furylfulgide*, $C_{22}H_{14}O_4$, formed by pouring cold acetyl chloride on to the dicarboxylic acid, crystallises from carbon disulphide in dark red prisms, which lose CS_2 on exposure to air; when free from carbon disulphide, it is dichromate-red, melts at 156°, is easily soluble in chloroform or benzene, and dissolves in concentrated sulphuric acid to form a green solution which becomes brown, and on dilution with water deposits a greenish-blue, flocculent precipitate.

αδ-Difurylfulgenic acid (difurfurylidenesuccinic acid),

$$C_4OH_3\cdot CH:C(CO_2H)\cdot C(CO_2H):CH\cdot C_4OH_3,$$

is obtained by treating a mixture of 3 mols. of furfuraldehyde and 1 mol. of ethyl succinate in alcoholic solution with 2 mols. of sodium ethoxide in a yield of 15 per cent. of the theoretical; it melts at 227—228° (217—225°: Fichter and Scheuermann, Abstr., 1901, i, 479; 185—187°: Titherley and Spencer, Trans., 1904, **85**, 190).

αδ-Difurylfulgide (difurfurylidenesuccinic anhydride) forms brownish-red, rhombic crystals, softens at 197°, and melts at 204° (187°: Titherley and Spencer, *loc. cit.*, p. 188). G. Y.

Diphenyl-*o*-phenoxylenedihydroanthracene. Fritz Ullmann and Jacob Tscherniak (*Ber.*, 1905, **38**, 4110—4111).—*2'-Hydrofluoranyldiphenylcarbinol*, $O<\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}>CH\cdot C_6H_4\cdot CPh_2\cdot OH$, prepared by the action of bromobenzene and magnesium on methyl hydrofluoranate (Meyer, Abstr., 1895, i, 291), $O<\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}>CH\cdot C_6H_4\cdot CO_2Me$, separates from benzene in colourless crystals and melts at 196°. By the action of acetic and sulphuric acids, it is converted into 10 : 10-*diphenyl-1 : 9-o-phenoxylenedihydroanthracene*,  $\begin{array}{l}C_6H_4\cdot CH-C_6H_4\\ |\qquad\quad |\qquad\quad |\\ CPh_2\cdot C_6H_3\cdot O\end{array}$, which separates in colourless crystals and melts at 325°. T. M. L.

Salts of the Alkaloid Cinchonamine. Bernard F. Howard and F. Perry (*J. Soc. Chem. Ind.*, 1905, **24**, 1281—1283).—The cinchonamine used in the investigation was obtained from a sample of the crude nitrate which had been precipitated from the alkaloid of the bark of *Remijia Purdeiana.* The crude salt was twice recrystallised from water and converted into the hydrochloride, in which form it was several times recrystallised; on precipitating the base and recrystallising it from acetone, it was obtained as a perfectly white, crystalline product. Cinchonamine hydrochloride, $C_{19}H_{24}ON_2,HCl$, crystallises from the acid solution in soft, almost white, glistening laminæ. A hot saturated neutral solution of the hydrochloride cooled to 27° deposits cubical crystals of a monohydrated salt. A dihydrochloride could not be obtained. The hydrobromide was prepared in a manner exactly similar to the hydrochloride and was found to be anhydrous; it is very slightly soluble in cold water. The hydriodide prepared by double decomposition of a salt of cinchonamine with potassium iodide or by boiling the alkaloid with 5 per cent. hydriodic acid crystallises in shining, slightly yellow plates; on exposure to dry air, it loses hydrogen iodide; it is almost insoluble in cold water, but is fairly soluble at higher temperatures. The platinichloride forms a very insoluble, semicrystalline, yellow solid. The *salicylate* prepared by neutralising a warm solution of salicylic acid with cinchonamine forms a resinous mass which crystallises from dilute aqueous solutions in thick, colourless prisms, which are very readily soluble in acetone. The sulphate was obtained by neutralising an alcoholic solution of the alkaloid with dilute sulphuric acid at a temperature just below the boiling point of alcohol; on rendering the neutral solution just acid and cooling, it was deposited in small needles; it is extremely soluble in water and is practically insoluble in absolute alcohol; it is very soluble in pyridine and crystallises from it with one molecule of the solvent. The acid sulphate, $C_{19}H_{24}ON_2,H_2SO_4$, is best prepared by dissolving the sulphate in a small quantity of water at the temperature of the boiling water-bath and stirring in a molecular quantity of dilute sulphuric acid; on slow evaporation in a vacuum, the solution deposits large, truncated octahedra. The *picrate* obtained as a yellow, amorphous powder by adding a cold aqueous solution of picric acid to the hydrochloride melts at 54° and contains $\frac{1}{2}H_2O$. Solubility curves are given for the haloid salts. P. H.

Nicotine and its Specific Rotation. I. FLORIAN RATZ. (*Monatsh.*, 1905, **26**, 1241—1252).—The author has purified two samples of nicotine of different origins by fractional distillation under 20 mm. pressure, and obtained two fractions, having $[\alpha]_D$ $-163·19°$ and $-166·77°$ at 20° respectively. The specific rotation of these fractions was not altered by further fractional distillation, but on conversion of each into the zincochloride, fractional crystallisation of this, and liberation and fractional distillation of the base, two specimens of pure nicotine were obtained. This boils at 246·2° under 719·8 mm. pressure, and has the sp. gr. 1·00924—1·00925 at 20°/4° and $[\alpha]_D$ $-169·22°$ to $-169·54°$ at 20°.

Nicotine zincochloride, $C_{10}H_{14}N_2,2HCl,ZnCl_2,H_2O$, is soluble in two parts of water, or 4—4·5 parts of 60 per cent. alcohol, or in 0·1 or 0·35 part of the boiling solvents respectively.

A table is given showing the sp. gr. and the specific rotation of nicotine as found by a number of authors. The different figures obtained previously must be due to the presence, in varying amounts, of an impurity which is removed only partly by fractional distillation; the nature of this the author proposes to investigate. G. Y.

Scopolamine and Scopoline. ERNST SCHMIDT (*Arch. Pharm.*, 1905, **243**, 559—583. Compare Abstr., 1892, 1255; 1895, i, 158; 1898, i, 499; 1903, i, 51).—Numerous attempts to obtain reactions which would correspond with the presence of ketonic oxygen in scopoline, $C_8H_{13}O_2N$, gave no positive result. Further, it was not found possible to reduce scopoline in either acid, neutral, or alkaline solution; neither could a compound with hydrocyanic acid be obtained; nor was a benzylidene derivative formed when scopoline and benzaldehyde were allowed to remain in acetic acid solution saturated with hydrogen chloride, as happens with substances which contain a $CH_2{\cdot}CO$ group (Willstätter, Abstr., 1898, i, 160).

By methylating scopoline (Luboldt, Abstr., 1898, i, 499), a small quantity was obtained of a crystalline *methylscopoline* which melted at 69—70°; it was analysed in the form of its *aurichloride*,

$$C_9H_{15}O_2N,HAuCl_4,$$

which melts at 154°.

When scopoline is allowed to remain with hydrogen peroxide, it yields a product which melts and decomposes at 122° and forms a crystalline *hydrochloride*, $C_8H_{13}O_3N,HCl$; probably this product is an *oxide*, the NMe group having been converted into NMeO. Scopoline is oxidised but very slowly by a boiling solution of chromic and sulphuric acids; the products are scopoligenine, $C_7H_{11}O_2N$, pyridine methosulphate, methylamine, and carbon dioxide.

[With RUDOLF GAZE.]—Bromine, either in chloroform solution or in the form of vapour, converts scopoline partially into scopoligenine; in the latter case, a small quantity was also obtained of a substance melting at 110—113°, probably a *bromo*-derivative of scopoline.

Scopoligenine yields unsaturated hydrocarbons and pyridine when it is heated with zinc dust in a current of hydrogen gas.

When hydrobromoscopoline hydrobromide is boiled with phosphorus tribromide and the product reduced with zinc and dilute sulphuric acid, hydroscopolidine is formed; this was analysed in the form of its *aurichloride*, $C_8H_{15}N,HAuCl_4$, which melts at 204—206°.

Hydriodoscopoline hydriodide melts at 196°. The *aurichloride* of *hydroscopoline*, $C_8H_{15}O_2N,HAuCl_4$, which is obtained by reducing hydrobromoscopoline (Abstr., 1903, i, 51), melts at 200—201°.

New varieties of the platinichloride and aurichloride of scopoline, respectively anhydrous and with H_2O, are described; these melt practically at the same temperature as the salts known already. C. F. B.

Modern Theories of Double Linkings and the Constitutional Formula of Pyrrole. GIACOMO CIAMICIAN (*Gazzetta*, 1905, **35**, ii, 384—393).—The author discusses the various formulæ which have been proposed for pyrrole, in which, as he has already pointed out (Abstr., 1893, i, 602), two valencies of the nitrogen atom exist in a latent condition. On the basis of Thiele's theory of partial valencies, he supposes that in thiophen, pyrrole, and furan the partial valencies of the group $-CH{\vdots}CH{\cdot}CH{\vdots}CH-$ are more or less satisfied by the latent valencies of the sulphur, nitrogen, and oxygen respectively, the extent of this neutralisation being greatest with sulphur and least with oxygen (see also Abstr., 1905, i, 80). T. H. P.

Compounds of Copper Salts with Pyridine and Quinoline. PAUL PFEIFFER and V. PIMMER (*Zeit. anorg. Chem.*, 1905, **48**, 98—111). —The following additive compounds of copper nitrate and pyridine have been prepared. $Cu(NO_3)_2,2C_5H_5N$, a light blue powder; $Cu(NO_3)_2,3C_5H_5N$, azure-blue crystals; $Cu(NO_3)_2,4C_5H_5N$, violet plates; $Cu(NO_3)_2,6C_5H_5N$, small, cobalt-blue crystals. The tetrapyridine compound is readily formed from its components; with excess of the base, it forms the hexapyridine compound, whereas it yields the di- and tri-pyridine compounds when heated carefully. The *compounds* $Cu(NO_3)_2,2C_5H_5N,2H_2O$ and $Cu(NO_3)_2,6C_5H_5N,3H_2O$ have also been prepared; the former occurs in light blue plates, whilst the latter has a violet-blue colour.

Diquinoline cupric nitrate, $Cu(NO_3)_2,2C_9H_7N$, prepared directly from its components, crystallises in transparent, indigo-blue needles.

Dipyridine cupric bromide, $CuBr_2,2C_5H_5N$, prepared from its components, occurs in green needles; with excess of the base, it yields *hexapyridine cupric bromide*, $CuBr_2,6C_5H_5N$, as a blue, crystalline mass. *Pyridinium cupric bromide*, $Cu(C_5H_6N)_2Br_4$, prepared by dissolving the dipyridine additive compound in hydrobromic acid, forms lustrous, reddish-black, prismatic crystals; the corresponding quinolinium compound, $Cu(C_9H_8N)_2Br_4,3H_2O$, prepared by a similar method, crystallises in black plates. G. S.

Aminoacetals and Aminoaldehydes. II. ALFRED WOHL (*Ber.*, 1905, **38**, 4154—4157. Compare Abstr., 1901, i, 513).—A summary of the results contained in the three following abstracts. Aminoaldehydes and their substitution derivatives are best purified in the form of their platinichlorides; the free aldehydes very readily undergo condensation, and in only a few cases have they been obtained pure by reducing to a minimum the decomposing action of heat, alkali, and water. C. S.

γ-Aminobutyraldehyde and Pyrrolidine. ALFRED WOHL, KURT SCHÄFER, and A. THIELE (*Ber.*, 1905, **38**, 4157—4161).—γ-Aminobutyraldehyde diethylacetal is conveniently obtained by the interaction of β-chloropropaldehyde diethylacetal, sodium ethoxide, and dry hydrogen cyanide in alcoholic solution at 118—122° for two days, the product being subsequently reduced with sodium and absolute alcohol. *γ-Aminobutyraldehyde*, $NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CHO$, obtained by the decomposition of the acetal by a dilute solution of oxalic acid, forms a syrup which still contains oxalic acid. The *platinichloride*,

$$(C_4H_9ON)_2,H_2PtCl_6,$$

is an unstable, crystalline substance.

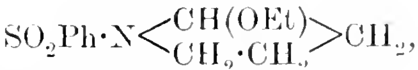
γ-Formylaminobutyraldehyde diethylacetal,

$$CHO{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH(OEt)_2,$$

prepared from ethyl formate and the acetal base, boils at 170° under 14 mm. pressure and is soluble in water or the usual organic solvents.

γ-Formylaminobutyraldehyde, $CHO{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CHO$, is obtained in an impure state by the decomposition of the acetal with oxalic acid. The *platinichloride*, $(C_5H_9O_2N)_2,H_2PtCl_6$, melts and decomposes at 176°.

1-Benzenesulphonyl-2-ethoxypyrrolidine,



$$SO_2Ph{\cdot}N{<}\begin{matrix}CH(OEt)\\CH_2{\cdot}CH_2\end{matrix}{>}CH_2,$$

obtained by the action of benzenesulphonic chloride on an aqueous-alcoholic solution of γ-aminobutyraldehyde diethylacetal and treatment of the oil so produced with a 5 per cent. alcoholic potash, is a crystalline substance which melts at 76—78° and distils without decomposition. It is insoluble in water, but dissolves in ordinary organic solvents; it is reduced to pyrrolidine by sodium and hot amyl alcohol. C. S.

Hydrogenated Pyridine-aldehydes. ALFRED WOHL, W. HERTZBERG, and M. S. LOSANITSCH (*Ber.*, 1905, 38, 4161—4169).—*β-Iminodipropaldehyde tetraethylacetal*, $NH[CH_2{\cdot}CH_2{\cdot}CH(OEt)_2]_2$, obtained by heating under pressure β-chloropropaldehyde diethylacetal (1 part) with a cold saturated solution of ammonia in alcohol (6 parts) at 118—120° for not more than nine hours, is a colourless, viscous liquid inclining to yellow: it boils at 157° under 15 mm. pressure, has a basic odour, is somewhat soluble in water, dissolves in the ordinary organic solvents, and has a sp. gr. 0·9466 at 15°. Dilute oxalic, hydrochloric, or sulphuric acid hydrolyses it to the extent of 88 per cent. Cold concentrated hydrochloric acid causes the formation of a syrup which was identified as *Δ^3-tetrahydropyridine-3-aldehyde* in the form of the *hydrochloride* of its *nitrophenylhydrazone*,

$$\begin{array}{l} HCl.NH{-}CH_2{-}C{\cdot}CH{:}N_2H{\cdot}C_6H_4{\cdot}NO_2, \\ \quad\;\;\, CH_2{\cdot}CH_2{\cdot}CH \end{array}$$

a hygroscopic, reddish-yellow substance which sinters at 173·5° and melts with decomposition at 251°.

β-Ethyliminodipropaldehyde tetraethylacetal,

$$NEt[CH_2{\cdot}CH_2{\cdot}CH(OEt)_2]_2,$$

obtained from ethylamine and β-chloropropaldehyde diethylacetal in benzene solution at 135—140°, is a colourless, viscous oil which boils at 159° under 13 mm. pressure; it is sparingly soluble in water and is miscible with the ordinary organic solvents. The *platinichloride*, $(C_{16}H_{35}O_4N)_2,H_2PtCl_6$, separates from dilute alcohol in yellow, octahedral crystals which melt and decompose at 92—93° (corr.).

1-Ethyl-Δ^3-tetrahydropyridine-3-aldehyde hydrochloride,

$$C_5NH_7Et{\cdot}CHO,HCl,$$

is obtained from the acetal by the action of cold concentrated hydrochloric acid. It separates from dilute alcohol in long, colourless crystals which melt at 208° (corr.), shows reducing properties, and gives a reddish-brown coloration with concentrated sulphuric acid and phenol or β-naphthol. The *platinichloride* forms yellow cubes which melt and decompose at 190°. The *hydrochloride* of the *nitrophenylhydrazone* separates from dilute alcohol in reddish-yellow, hygroscopic needles which melt and decompose at 263°. The *hydrochloride* of the *oxime* forms long, colourless needles which melt at 248—249° (corr.). The free *oxime*, which is not produced by mixing its components, is obtained from the hydrochloride by the action of potassium carbonate; it crystallises in white scales and melts at 134° (corr.). The *acetate* of the oxime, obtained by the action of acetic anhydride and sodium acetate on the hydrochloride, boils at 102—105° under 0·1 mm. pressure. Thionyl chloride converts the hydrochloride of the oxime into the *hydrochloride* of the *nitrile*, $C_5NH_7Et{\cdot}CN,HCl$, which separates from dilute alcohol in white needles melting at 265—266° (corr.).

4-Chloro-1-ethylpiperidine-3-aldehyde diethylacetal,

$$CH_2\!\left<\begin{matrix} NEt{-}{-}CH_2 \\ CH_2{\cdot}CHCl \end{matrix}\right>\!CH{\cdot}CH(OEt)_2,$$

prepared by the action of hydrogen chloride on the hydrochloride of 1-ethyl-Δ^3-tetrahydropyridine-3-aldehyde dissolved in absolute alcohol, is a colourless oil which boils at 79—80° under 0·05 mm. pressure. Its reduction by sodium and absolute alcohol produces 1-*ethylpiperidine-3-aldehyde diethylacetal*, which is a colourless oil boiling at 63—65° under 0·04 mm. pressure. C. S.

Free Aminoaldehydes. ALFRED WOHL and M. S. LOSANITSCH (*Ber.*, 1905, **38**, 4170—4172).—1-*Ethyl*-Δ^3-*tetrahydropyridine-3-aldehyde*, obtained from its hydrochloride (see preceding abstract) by the action of solid potassium carbonate, is a colourless, oily liquid with a basic stupefying odour; it boils at 52—54° under 0·06 mm. pressure, has an alkaline reaction and reducing properties, and is resinified by potassium hydroxide.

1-*Ethylpiperidine-3-aldehyde* is obtained in small quantity from the corresponding acetal (*loc. cit.*) by the action of strong hydrochloric acid with subsequent addition of potassium carbonate to the cold diluted solution. It is a colourless oil which boils at 40° under 0·2 mm. pressure; it has a burning taste, fumes with hydrochloric acid, and reduces Fehling's solution. In contact with air, it becomes resinous and insoluble in water. The *platinichloride* crystallises in octahedra.

β-*Ethylaminopropaldehyde diethylacetal*, $NHEt\cdot CH_2\cdot CH_2\cdot CH(OEt)_2$, is a by-product in the preparation of the tertiary base (*loc. cit.*). It is a colourless, mobile oil with a basic odour and strongly alkaline reaction. It boils at 82·5—83·5° under 13 mm. pressure. When decomposed by strong hydrochloric acid, it yields the hydrochloride of the aminoaldehyde, $C_5H_{11}ON,HCl$, which melts at 265—265·5° (corr.) and reduces solutions of silver salts.

β-*Ethylaminopropaldehyde*, $(NHEt\cdot CH_2\cdot CH_2\cdot CHO)_3$, is obtained from the hydrochloride by the action of potassium carbonate as a slightly yellow oil, which reduces solutions of silver salts but not Fehling's solution, answers to Schiff's test, and forms with hydrochloric acid a hydrochloride identical with that from which it is prepared. The free aldehyde is remarkably stable, retaining its properties unchanged after being heated in a vacuum to 180°. C. S.

Reciprocal Stereochemical Influences. HANS MEYER (*Monatsh.*, 1905, **26**, 1303—1310).—Two similar or dissimilar groups which influence each other so that they act as if only one group were present, the author terms "conjugated groups." Typical examples of substances containing "conjugated groups" are the 2- and 4-aminopyridines and the 2- and 4-aminoquinolines, in which the two basic groups influence each other so that salts are formed with only 1 mol. of hydrochloric acid. On treatment with nitrous acid, these bases behave as stable, aliphatic amines.

In 4-aminonicotinic acid, the carboxyl group, and in 4-aminolutidinic acid one of the two carboxyl groups, is partially neutralised by the "conjugated groups"; these acids are therefore *pseudo*-betaines (Abstr., 1904, **25**, 490).

On the other hand, in the 3-aminopyridines, 7-aminoquinoline, and 5- and 8-amino*iso*quinoline, the tertiary nitrogen and the amino-group have no stereochemical influence on each other, and these bases form salts with 2 mols. of hydrochloric acid, and when diazotised, behave as aromatic amines.

Similarly, whilst the 3-hydroxypyridines react normally, the 2- and 4-hydroxypyridines (2- and 4-pyridones) and the 2- and 4-hydroxyquinolines do not give the typical reactions. Thus the 2- and 4-pyridones do not yield nitroso-derivatives, cannot be acetylated, do not react normally with phenylcarbimide (Goldschmidt and Meissler, Abstr., 1890, i, 499), and have only feeble salt-forming properties. Claus has shown that on bromination of carbostyril the "conjugated group" exerts no directive influence (Abstr., 1896, i, 449). G. Y.

Action of Diazomethane on Pyridones and Hydroxypyridinecarboxylic Acids. HANS MEYER (*Monatsh.*, 1905, **26**, 1311—1329. Compare preceding abstract).—Whilst 2-pyridone is converted into 2-methoxypyridine only slowly and partially by the action of diazomethane, this reagent interacts energetically with 3-hydroxypyridine, which must be a true hydroxy-compound forming 3-*methoxypyridine*; this yields a *mercurichloride*, which crystallises in slender, colourless needles and melts at 110°, and a *platinichloride*, which is obtained in yellowish-red crystals and melts at 182°.

The action of diazomethane on 4-pyridone leads to the formation of a mixture of 4-methoxypyridine and 1-methyl-4-pyridone. 4-*Methoxypyridine mercurichloride* crystallises in colourless needles and melts at 191°. Carbostyril interacts with diazomethane to form 2-methoxyquinoline and not the *N*-methyl derivative.

The action of methyl iodide on 6-hydroxynicotinic acid in aqueous alkaline solution leads to the formation of 6-keto-1-methyl-1 : 2-dihydropyridine-3-carboxylic acid, which melts at 238—239° (compare von Pechmann and Welsh, Trans., 1885, **47**, 150; Abstr., 1885, 174). This differs from all 1-methylpyridinecarboxylic acids investigated previously, as owing to the negative influence of the keto-group on the methylimino-group it does not form the betaine, and can be titrated with *N*/10 potassium hydroxide. When treated with diazomethane, it yields the *methyl* ester, which crystallises in long, glistening needles and melts at 139°.

The action of diazomethane on 6-hydroxynicotinic acid leads to the formation of a mixture of derivatives consisting of 88·5 per cent. of methyl 6-keto-1-methyl-1 : 2-dihydropyridine-3-carboxylate and 11·5 per cent. of *methyl* 6-*methoxynicotinate*, $OMe\cdot C_5NH_3\cdot CO_2Me$, which crystallises in soft needles and melts at 122°, whereas diazomethane and methyl 6-hydroxynicotinate interact to form methyl 6-keto-1-methyl-1 : 2-dihydropyridine-3-carboxylate only.

Methyl 2-hydroxycinchonate is formed from the acid by the action of thionyl chloride or sulphuric acid and methyl alcohol, or together with methyl 2-methoxycinchonate by the action of diazomethane. It crystallises in glistening, colourless needles, melts at 242°, sublimes at 240—250°, and distils apparently without change. *Methyl 2-methoxycinchonate* crystallises in needles, melts at 120°, and has an odour of orange blossoms. When boiled with 2 per cent. aqueous sodium hydroxide, *propionylisatin*, which is formed by boiling isatin with propionic anhydride and melts at 141°, yields 2-hydroxy-3-methylcinchonic acid, $OH·C_9NH_4Me·CO_2H$; this separates from water in colourless crystals, melts at 315—317°, and when treated with thionyl chloride and methyl alcohol or with diazomethane yields *methyl 2-hydroxy-3-methylcinchonate*, which crystallises in long, slender needles and melts at 174—175°. Prolonged treatment with diazomethane had no further action on the methyl ester.

Chelidamic acid interacts energetically with diazomethane, forming the *dimethyl* ester, $OH·C_5NH_2(CO_2Me)_2$, which crystallises in long needles, melts at 125°, and is only sparingly soluble in ether.

The author discusses the constitution of comenamic acid (compare Lapworth and Collie, Trans., 1897, **71**, 843; Peratoner, Abstr., 1902, i, 493), and concludes that it is 4 : 5-dihydroxypyridine-2-carboxylic acid. It does not interact with thionyl chloride (compare Abstr., 1902, i, 31), but when treated with diazomethane yields *methyl 4-hydroxy-5-methoxypyridine-2-carboxylate*, melting at 118°. G. Y.

Formation from Furfuraldehyde of Colouring Matters derived from Pyridine. Wilhelm König (*J. pr. Chem.*, 1905, [ii], **72**, 555—562. Compare Abstr., 1904, i, 449, 817; Zincke, Heuser, and Möller, Abstr., 1904, i, 921; Zincke and Mühlhausen, this vol., i, 33).—The *hydrobromide* of α-hydroxyglutaconaldehydedianilide, $NHPh·CH:CH·CH:C(OH)·CH(OH)·NHPh,HBr$, is formed by heating aniline with furfuraldehyde in alcoholic solution on the water-bath, and, after cooling, adding hydrobromic acid of sp. gr. 1·48, diluted with alcohol. It crystallises from acetic acid in prisms which have a deep blue lustre, melts at 164—165°, and dyes silk and tannin mordanted cotton-wool deep red or unmordanted cotton-wool rose-red. When heated with nitrobenzene at 150°, it decomposes into aniline and 3-hydroxy-1-phenylpyridinium bromide, which crystallises in white needles containing H_2O and melts at 129° (compare Zincke and Mühlhausen, *loc. cit.*). The picrate, $C_{17}H_{12}O_8N_4$, crystallises in slender, yellow needles and melts at 219°.

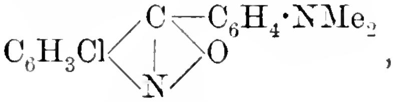
The *hydrobromide* of α-hydroxyglutaconaldehydedi-*p*-phenetidide, $C_{21}H_{26}O_4N_2,HBr$, formed from *p*-phenetidine and furfuraldehyde by the same method as the dianilide, crystallises in glistening, blue prisms, melts at 157—158°, and dyes silk and unmordanted cotton-wool the rhodamine colour, but not fast. The free *base* is obtained as a yellow, oily mass. When heated with nitrobenzene, it yields *3-hydroxy-1-p-ethoxyphenylpyridinium bromide*, $C_{13}H_{14}O_2NBr,H_2O$, which crystallises in colourless, iridescent leaflets and melts at 167—168°. The *picrate* forms yellow needles and melts at 207°. G. Y.

Dyes derived from Furfuraldehyde. Walter Dieckmann and Ludwig Beck [and, in part, Bruno Szelinski] (*Ber.*, 1905, **38**, 4122—4125. Compare Zincke and Mühlhausen, this vol., i, 33; König, preceding abstract).—Hydroxyglutaconaldehydedianilide hydrobromide, $NHPh·CH:CH·CH:C(OH)·CH:NPh,HBr,H_2O$, prepared either by the action of aniline and aniline hydrobromide on furfuraldehyde or by the action of aniline and cyanogen bromide on 3-hydroxypyridine, melts and decomposes at 166° and is converted by heating with alcohol and hydrochloric acid into 3-hydroxy-1-phenylpyridinium chloride, $OH·C_5NH_4PhBr$, which melts and decomposes at

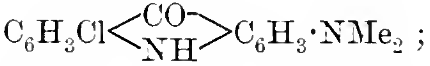
210° and yields a *picrate* melting and decomposing at 218—221° and a *platinichloride* melting and decomposing at 199°; the identity of the two preparations is thus fully demonstrated.

Similar evidence was obtained in the case of the *p*-chloroaniline derivatives. *Hydroxyglutaconaldehydedi*-p-*chloroanilide hydrochloride*, $C_6H_4Cl{\cdot}NH{\cdot}CH{:}CH{\cdot}CH{:}C(OH){\cdot}CH{:}N{\cdot}C_6H_4Cl,HCl$, resembles the dianilide hydrochloride and melts and decomposes at 167°. 3-*Hydroxy*-1-p-*chlorophenylpyridinium chloride*, $OH{\cdot}C_5NH_4Cl{\cdot}C_6H_4Cl$, crystallises from water in long, colourless needles and melts and decomposes at 221°. The *platinichloride* crystallises from hot water in orange-yellow needles and melts and decomposes at 217°. T. M. L.

Action of *o*-Nitrobenzaldehyde on Dimethylaniline in Presence of Hydrochloric Acid. THEODOR ZINCKE and WILHELM PRENNTZELL (*Ber.*, 1905, **38**, 4116—4122).—*o*-Nitrobenzaldehyde and dimethylaniline, which yield a triphenylmethane compound when acted on by zinc chloride, give, when acted on by concentrated hydrochloric acid at 110—115°, a *compound*, $C_{15}H_{13}ON_2Cl$, which is formulated as an anthranil derivative,



but might possibly be an acridone compound,



$$C_6H_3Cl{<}\begin{smallmatrix}CO\\NH\end{smallmatrix}{>}C_6H_3{\cdot}NMe_2\ ;$$

it crystallises from hot alcohol in yellow needles, from acetone in stout, reddish-yellow needles, and melts at 162—163°; its dilute alcoholic and ethereal solutions show a very strong fluorescence, similar to that of fluorescein; concentrated solutions are yellow; it is stable towards alkali hydroxides and does not lose chlorine, but has slight basic properties. The *hydrochloride* forms colourless flakes, the *nitrate* and *sulphate* colourless needles; the *platinichloride*, $(C_{15}H_{13}ON_2Cl)_2,H_2PtCl_6$, crystallises in minute, yellow scales, is insoluble in water, and decomposes above 200°; the *methiodide*, $C_{15}H_{13}ON_2Cl,MeI$, crystallises from hot alcohol in glistening scales, melts at 184° liberating methyl iodide, and fluoresces in alcoholic solution.

Reduction by means of zinc and acetic acid gives a compound formulated as 5-*chloro*-2-*amino*-4′-*dimethylaminobenzophenone*,

$$NH_2{\cdot}C_6H_3Cl{\cdot}CO{\cdot}C_6H_4{\cdot}NMe_2,$$

which crystallises in minute, yellow needles and melts at 185°. The *hydrochloride* crystallises from dilute hydrochloric acid in colourless, glistening tablets, but is decomposed by water or alcohol. The *acetyl* derivative crystallises from dilute alcohol in yellow, glistening needles and melts at 132°. The ketone is reduced by hydrogen iodide and phosphorus at 190—200° to 2 : 4′-diaminodiphenylmethane (Stadel, Abstr., 1895, i, 233), which crystallises from ether in transparent tablets, melts at 88—89°, and is readily converted into diphenylmethane. The *hydrochloride* crystallises in small, colourless needles. The acetyl derivative separates from alcohol in white, tabular crystals melting at 208°, or in small, glistening needles melting at 218°; only the latter modification is described by Stadel. T. M. L.

Phenylhydrazine as a Reducing Agent in Organic Chemistry. Giuseppe Plancher (*Gazzetta*, 1905, **35**, ii, 460—463).—Polemical. A reply to Oddo and Puxeddu (Abstr., 1905, i, 842).

T. H. P.

Phenylethylidenehydrazine. Georg Lockemann and Otto Liesche (*Annalen*, 1905, **342**, 14—50).—Phenylethylidenehydrazine, that is, acetaldehydephenylhydrazone, was used in the preparation of acraldehyde as a means of recognising acetaldehyde (Abstr., 1905, i, 570). It has been shown by Fischer (Abstr., 1896, i, 361) to exist in two or three mutually convertible isomeric forms. A list is given of the phenylhydrazones of aldehydes or ketones or ketonic acids, of osazones, of diketones, and other similar hydrazones which exhibit isomerism. This isomerism has been variously regarded as a structural or steric isomerism, but the explanation given by Hantzsch, and based on the latter type of isomerism, is regarded as the most adequate.

The conditions under which the two forms of the acetaldehydephenylhydrazone are stable have been investigated. Fischer (*loc. cit.*) obtained a β-form (m. p. 63—65°), which was transformed by alcoholic sodium hydroxide into the α-form, melting at 98—101°; the latter then passed slowly into a third variety melting at 80°. It is now found that this substance exists in two modifications; the stable *α-variety* melts at 98—101°, whilst the labile *β-form* melts at 57°. The β-hydrazone gradually changes into the α-form, but the transformation is hastened by the action of bases, such as sodium hydroxide or ammonia, and also by various salts. Crystallisation from alkaline 75 per cent. alcohol is the most effectual method. The change from the α- into the β-form also takes place in certain solvents, but is momentarily effected by treatment with aqueous sulphurous acid. The depression of the freezing point of the α-modification does not appear to be due to a conversion into a third form, but to decomposition, oxidation, &c. Fischer's isomeride (m. p. 63—65°) is probably an amorphous mixture of the α- and β-hydrazones.

Acetaldehydephenylhydrazone is prepared by adding molten phenylhydrazine to an ice-cold solution of acetaldehyde in light petroleum. The product, which is white, can only be kept in an atmosphere free from alkaline or acid vapours; it melts usually at 51—57°, although higher melting points (98°) have been observed. On crystallisation from 75 per cent. alcohol containing a trace of sodium hydroxide, prismatic crystals of the α-modification are obtained.

The β-modification is obtained by adding aqueous sulphurous acid either to a 75 per cent. alcoholic solution of the α-hydrazone or by moistening the crystals. The use of a stronger acid, hydrochloric or nitric, brings about the transformation, but at the same time causes some decomposition. Carbon dioxide attacks the α-modification slowly, but does not convert it into the β-form. Even in a completely neutral medium, such as air, the β-modification becomes coloured, and the melting point rises.

Indifferent solvents cause the transformation of either form into the other, but in no case can a complete transformation be effected by simple recrystallisation. The melting point of the β-form may be somewhat raised by recrystallisation or that of the α-form somewhat lowered.

Both isomerides show the same behaviour towards benzoyl chloride. Dibenzoylphenylhydrazine (m. p. 177—178°) is formed when an aqueous suspension of the hydrazone is treated with benzoyl chloride and sodium hydroxide; at the same time *tribenzoylphenylhydrazine*, $C_{27}H_{20}O_3N_2$, is formed; it can be prepared by repeated treatment of phenylhydrazine with benzoyl chloride in ethereal solution in the presence of sodium hydroxide, and crystallises in rhombic plates melting at 200—201°. Both the α- and β-hydrazones yield the same *β-benzoyl-β-phenyl-α-ethylidenehydrazine*, $CHMe{:}N{\cdot}NPhBz$, when the benzoylation is carried out in pyridine solution; it crystallises in rectangular plates or cubes melting at 89—90°, and is reduced by zinc dust and acetic acid to benzanilide. It does not condense under the action of phosphoric oxide or zinc chloride to a diphenylpyrazole.

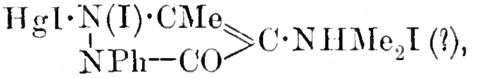
It is thought that the isomerism of acetaldehydephenylhydrazone is not explicable from a stereochemical standpoint, but rather is better accounted for as a case of tautomerism. K. J. P. O.

Diphenylhydrazine, Hydrazobenzene, and Benzylaniline, and Miscibility of the last two with Azobenzene, Stilbene, and Dibenzyl in the Solid State. F. M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, **8**, 466—474).—The following crystallographic constants were determined: *as*-diphenylhydrazine, triclinic [$a:b:c = 0·7698:1:0·5986$; $\alpha = 89°24'$, $\beta = 137°28·5'$, $\gamma = 90°4·5'$]; hydrazobenzene, rhombic [$a:b:c = 0·9787:1:1·2497$]; benzylaniline, monoclinic [$a:b:c = 2·1076:1:1·6422$; $\beta = 76°36·5'$].

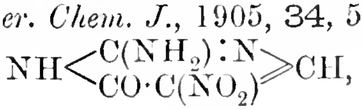
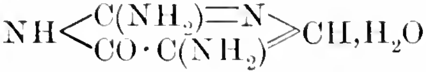
Bruni and Gorni (Abstr., 1899, ii, 407, 732) and Garelli and Calzolari (Abstr., 1899, ii, 732; 1900, ii, 65) have concluded from freezing-point observations that mixed crystals are formed between dibenzyl, stilbene, tolane, and azobenzene, the groups $-CH_2{\cdot}CH_2-$, $-CH{:}CH-$, $-C{:}C$. and $-N{:}N-$ being capable of mutual replacement in an isomorphous series, a conclusion which has been confirmed by the crystallographic measurements of Boeris (*Atti Soc. Ital. Sci. Milano*, 1900, **39**, 111—123). It has therefore been suggested that if two aromatic substances can form mixed crystals, their hydro-products can do the same. This conclusion is contradicted by the marked contrast between hydrazobenzene (rhombic) and azobenzene (monoclinic), which are not isomorphous, do not form mixed crystals, and give the normal V-shaped melting-point curve; the group $-NH{\cdot}NH-$ must therefore be excluded from the above series. Benzylaniline, containing the mixed group $-CH_2{\cdot}NH-$, might be expected to fall in with the rest of the series; actually, although not isomorphous with azobenzene, a rearrangement of the indices gives very similar values for $a:b$ and for β, but different values for $c:b$; the relationship is therefore morphotropic but not isomorphous. T. M. L.

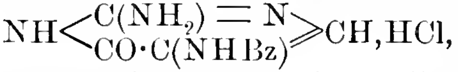
Action of Nessler's Solution on Antipyrine, Pyramidone, Antifebrin, and Exalgin. PAUL N. RAIKOW and CHR. KÜLÜMOW (*Chem. Centr.*, 1905, ii, 1595; from *Oesterr. Chem. Zeit.*, [ii], **8**, 445—448. Compare Schuyten, Abstr., 1898, i, 452; Ville and Astre, Abstr., 1900, i, 362, 411).—The author has succeeded in preparing mercuric iodide compounds of antipyrine, pyramidone, antifebrin, and exalgin by using alkaline solutions of mercuric iodide.

"*Antipyrine oil*" forms a bright yellow, somewhat viscous liquid and has a sp. gr. 1·3518 at 19°; it is readily soluble in alcohol or acetone, less so in water, and insoluble in ether, carbon disulphide, chloroform, or alkalis. The aqueous solution is alkaline. The compound is decomposed when treated with water which has not been distilled, or by boiling the solution in distilled water, a white precipitate being formed in each case; hydrochloric and sulphuric acids also give precipitates. Antipyrine oil is not volatile and is decomposed when strongly heated. With concentrated sulphuric acid, it gives a red coloration, and on warming the mixture small, red crystals are formed and iodine liberated. By the action of hydrogen sulphide, silver nitrate, and an excess of silver nitrate on a solution of the oil in acetone, mercuric sulphide, mercuric iodide, and silver iodide are formed respectively; when heated with acetic acid, a compound,  $\mathrm{Hg}\left[\mathrm{N(I)}<\begin{matrix}\mathrm{NPh\cdot CO}\\ \mathrm{CMe{:}CH}\end{matrix}\right]_2$?, is formed, which crystallises in pale yellow, prismatic crystals, melts at 133°, and is decomposed by repeated crystallisation from glacial acetic acid. It is soluble in acetone, chloroform, or glacial acetic acid, but insoluble in cold water, ether, or carbon disulphide. When heated with water, it becomes deep yellow, but regains its original colour on cooling; the warm aqueous solution is neutral.

The *compound*  $\begin{matrix}\mathrm{HgI\cdot N(I)\cdot CMe}\\ \mathrm{NPh{-}{-}CO}\end{matrix}\!\geqslant\mathrm{C\cdot NHMe_2I}$ (?), formed by the action of Nessler's reagent on dimethylaminoantipyrine (pyramidone), crystallises from acetic acid in sulphur-yellow needles and melts at 170—172°; it is readily soluble in acetone or hot acetic acid, sparingly so in water, and insoluble in ether, chloroform, or benzene. The aqueous solution is neutral to litmus. Acetanilide (antifebrin) is only partially attacked by Nessler's reagent, a yellow mercuric iodide compound being formed which is insoluble in ether, chloroform, or alcohol, and is decomposed by water with liberation of mercuric iodide.

The yellow oil, "*exalgin oil*," $\mathrm{HgI\cdot NPhMeI\cdot COMe}$ or $\mathrm{Hg_2(NPhIMe\cdot COMe)_2,2HI}$, obtained by the action of Nessler's reagent on methylacetanilide (exalgin), gradually becomes darker; it is miscible with a small quantity of water. By the action of a large quantity of water on the oil, yellow mercuric iodide is formed, and the liquid becomes opaque; after a time, however, red mercuric iodide separates out and the liquid regains its transparency and becomes almost colourless. When water or ether is added to a solution of the oil in acetic acid, red mercuric iodide is formed. The oil is insoluble in carbon disulphide and is partially decomposed by light petroleum, regenerating its components; by the action of concentrated sulphuric or nitric acid, exalgin and iodine are formed. E. W. W.

Pyrimidines; 2:5-Diamino-6-oxypyrimidine. XII. TREAT B. JOHNSON and CARL O. JOHNS (*Amer. Chem. J.*, 1905, 34, 554—568).—5-*Nitro-2-amino-6-oxypyrimidine*,  $\mathrm{NH}<\begin{matrix}\mathrm{C(NH_2){:}N}\\ \mathrm{CO\cdot C(NO_2)}\end{matrix}\geqslant\mathrm{CH}$, obtained by the nitration of 2-amino-6-oxypyrimidine (*iso*cytosine) (Wheeler and Johnson, Abstr., 1903, i, 526), crystallises in groups of yellow, microscopic prisms, becomes brown at about 280°, does not decompose below 300°, and is insoluble in the usual organic solvents; when heated for four hours at 190—200° with dilute sulphuric acid, it is converted into nitrouracil. When 5-nitro-2-amino-6-oxypyrimidine is reduced with aluminium amalgam in presence of ammonia, 2 : 5-*diamino-6-oxypyrimidine*,  $\mathrm{NH}<\begin{matrix}\mathrm{C(NH_2){=}N}\\ \mathrm{CO\cdot C(NH_2)}\end{matrix}>\mathrm{CH,H_2O}$, is produced, which crystallises in large, radiating prisms, is very soluble in water, and is probably identical with the diamino-oxypyrimidine obtained by Kutscher (Abstr., 1903, i, 668) from the nucleic acid of yeast. The anhydrous base decomposes at about 245° and has no definite melting point. The *picrate*, *hydrochloride*, *nitrate*, and *sulphate* are described. When 2 : 5-diamino-6-oxypyrimidine is heated with 20 per cent. sulphuric acid for three hours at 130—140° in a sealed tube, it is partially converted into 2-*amino*-5 : 6-*dioxypyrimidine*, which crystallises from water in groups of microscopic prisms and does not decompose below 300°; its *picrate* is described.

2 : 5-Diamino-6-oxypyrimidine may also be prepared by heating 5-bromo-2-amino-6-oxypyrimidine with concentrated solution of ammonia or by the action of alcoholic ammonia on 5-amino-6-oxy-2-ethylthiolpyrimidine. When an aqueous solution of guanidine is heated with ethyl sodioformylhippurate, 2-*amino-6-oxy-5-benzoylaminopyrimidine hydrochloride*,  $\mathrm{NH}<\begin{matrix}\mathrm{C(NH_2){=}N}\\ \mathrm{CO\cdot C(NHBz)}\end{matrix}>\mathrm{CH,HCl}$, is produced, which crystallises from hot water in microscopic needles and decomposes at about 275°. By the action of benzaldehyde on 2-amino-6-oxypyrimidine, 6-*oxy-2-benzylideneaminopyrimidine*,

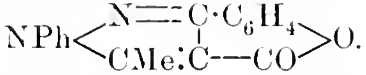
$$\mathrm{NH}<\begin{matrix}\mathrm{C(N{:}CHPh){:}N}\\ \mathrm{CO\text{———}CH}\end{matrix}>\mathrm{CH},$$

is obtained, which forms yellow crystals, decomposes at 238—242°, and is very stable towards nitric acid. When a solution of 2-amino-6-oxypyrimidine in acetic acid is treated with sodium nitrite, a *substance* is formed which crystallises in microscopic prisms, is very soluble in water, turns brown at about 280°, does not melt below 300°, and is probably an acetate of 2-amino-6-oxypyrimidine. E. G.

New General Method of Synthesising Pyrazole Derivatives.

GAETANO MINUNNI [in part with G. VASSALLO, RICCARDO CIUSA, and GUIDO LAZZARINI] (*Atti R. Accad. Lincei*, 1905, [v], 14, ii, 414—420).—On heating a mixture of equal quantities of benzaldehydephenylhydrazone and ethyl acetoacetate at 195—205°, a *substance*, $C_{21}H_{16}O_2N_2$, is obtained which crystallises from alcohol in white, nacreous laminæ melting at 140—140·5°, and is soluble in ether, light petroleum, or amyl alcohol, and very readily so in ethyl acetate, benzene, or chloroform. It dissolves in cold concentrated sulphuric acid, imparting to it an intense red coloration, and when boiled with concentrated potassium hydroxide solution is converted into a substance which separates from alcohol in white crystals melting at 112—113°. With bromine in chloroform solution, it gives a compound which crystallises from alcohol in long, white needles melting at 160°, and contains 20·5 per cent. of bromine. Later attempts to prepare the substance $C_{21}H_{16}O_2N_2$ from other samples of ethyl acetoacetate have proved fruitless, and its constitution has not been determined.

The condensation of benzaldehydephenylhydrazone and ethyl acetoacetate in presence of zinc chloride yields ethyl 1 : 3-diphenyl-5-methylpyrazole-4-carboxylate (Knorr and Blank, Abstr., 1885, 810). Similarly, the condensation of salicylaldehydephenylhydrazone with ethyl acetoacetate in presence of zinc chloride leads first to the formation of ethyl 1-phenyl-3-hydroxyphenyl-5-methylpyrazole-4-carboxylate, which loses one mol. of ethyl alcohol, giving the lactone of 1-phenyl-3-hydroxyphenyl-5-methylpyrazole-4-carboxylic acid,

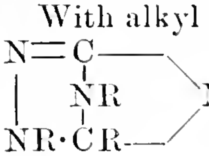


$$\mathrm{NPh}<\begin{matrix}\mathrm{N{=}C\cdot C_6H_4}\\ \mathrm{CMe{:}C{-}CO}\end{matrix}>\mathrm{O}.$$

By alcoholic potassium hydroxide solution, this lactone is transformed into the acid, which is readily reconverted into the lactone by heating or by the action of acid chlorides. The phenylhydrazone of *m*-(or *p*-)-nitrobenzaldehyde, when condensed with ethyl acetoacetate in presence of zinc chloride, yields ethyl 1-phenyl-3-*m*-(or *p*-)nitrophenyl-5-methylpyrazole-4-carboxylate. T. H. P.

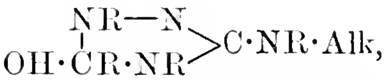
*endo*Iminotriazoles. II. Max Busch and Gustav Mehrtens (*Ber.*, 1905, **38**, 4049—4068. Compare Abstr., 1905, i, 307).—The action of aldehydes on triarylaminoguanidines leads to the formation of aminodihydrotriazoles,  $\begin{matrix}\mathrm{NR{-}N}\\ \mathrm{CHR\cdot NR}\end{matrix}>\mathrm{C\cdot NHR}$, which are decomposed by mineral acids and on oxidation yield *endo*iminotriazoles, which are formed also by the action of acetic and benzoic acids on triarylaminoguanidines in presence of phosphorus pentachloride, but not of the acids alone; they form sparingly soluble nitrates.

With alkyl haloids, the *endo*iminotriazoles form additive compounds,



$$\begin{matrix}\mathrm{N{=}C{-}}\\ \mathrm{NR}\\ \mathrm{NR\cdot CR{-}}\end{matrix}>\mathrm{NR,AlkX},$$

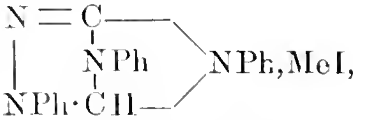
which yield carbinol bases,



$$\begin{matrix}\mathrm{NR{-}N}\\ \mathrm{OH\cdot CR\cdot NR}\end{matrix}>\mathrm{C\cdot NR\cdot Alk},$$

and when heated with potassium hydroxide are decomposed with rupture of the cyclic nucleus.

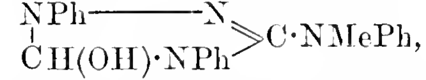
3-*Anilino*-1 : 4-*diphenyl*-4 : 5-*dihydro*-1 : 2 : 4-*triazole*,
$C_2N_3H_2Ph_2\cdot NHPh$,
formed by the action of formaldehyde on triphenylaminoguanidine in boiling alcoholic solution, crystallises in stout, white, glistening needles, melts at 128°, is easily soluble in chloroform, ether, benzene, or hot alcohol, and yields formaldehyde when heated with dilute sulphuric acid. When oxidised with alcoholic ferric chloride or sodium nitrite in alcoholic-acetic acid solution, it yields 1 : 4-diphenyl-3 : 5-*endo*anilodihydrotriazole, which the author terms "nitron." This forms a *picrate*, $C_{26}H_{19}O_7N_7$, which crystallises in sheaves of small needles and melts at 257—258°, and a *dichloride*, $C_{20}H_{16}N_4,2HCl$, which crystallises in glistening, white leaflets and commences to

decompose at 160°. The *methiodide*,  formed by heating nitron with an excess of methyl iodide in a reflux apparatus fitted with a mercury valve, crystallises from alcohol in yellow plates, or from water in glistening needles, melts at 211—213°, and has the conductivity $\mu_{272} = 85$ at 25°.

The aqueous solution of the methiodide becomes neutral immediately on addition of sodium hydroxide, but in dilute alcoholic solution the isomeric change from the strongly alkaline ammonium base first formed, into the carbinol base takes place more slowly, and is represented by the gradually diminishing alkalinity of the solution. The action of sodium hydroxide leads, further, to the hydrolysis of the carbinol base and formation of a red *azo*-compound, which on reduction with hydrogen sulphide yields *anilinodiphenylmethylguanidine*,

$$NHPh \cdot NH \cdot C(NPh) \cdot NMePh;$$

this crystallises in sheaves of needles, melts at 96—97°, is readily soluble in benzene or ether, and is oxidised in alcoholic solution by the air, becoming red.

The *carbinol* base (5-*hydroxy*-3-*methylanilino*-1 : 4-*diphenyl*-4 : 5-*dihydro*-1 : 2 : 4-*triazole*),  is prepared by treating the methiodide with aqueous ammonia; it forms a yellow powder, melts at 65°, is readily soluble in alcohol, ether, or benzene, and on treatment with nitric acid in dilute acetic acid solution forms the *methonitrate*, $C_{21}H_{19}N_4 \cdot NO_3$, which crystallises in glistening, clear, flat needles and melts at 160°. The *methopicrate*, $C_{21}H_{19}N_4,C_6H_2O_7N_3$, formed by the action of picric acid on the carbinol base in dilute acetic acid solution or on the methiodide in alcoholic solution, crystallises in long, glistening needles and melts at 193°.

The *additive* compound of nitron and benzyl chloride,

$$C_{27}H_{23}N_4Cl,H_2O,$$

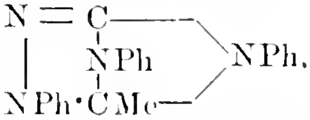
crystallises in clear, thick, tetragonal plates, sinters slightly at 180°, melts at 210°, is readily soluble in alcohol or warm water, forming neutral solutions, has the conductivity $\mu_{10} = 60$ at 25°, and exhibits the same behaviour as the methiodide on treatment with alkali hydroxides. The *hydrochloride*, $C_{27}H_{23}N_4Cl,HCl$, crystallises in colourless needles, softens at 150°, and melts and decomposes at 160°; the *nitrate*, $C_{27}H_{23}O_3N_5$, crystallises in white needles, sinters at 209°, and decomposes suddenly at a few degrees higher. The *carbinol* base (5-*hydroxy*-3-*benzylanilino*-1 : 4-*diphenyl*-4 : 5-*dihydro*-1 : 2 : 4-*triazole*), $C_{27}H_{24}ON_4$, formed by the action of aqueous ammonia on the chloride, crystallises in glistening, transparent, short, tetragonal prisms, melts at 153°, is only sparingly soluble in alcohol, ether, or benzene, and on treatment with alcoholic hydrogen chloride is converted into a mixture of the benzyl chloride additive compound and its hydrochloride.

Anilinodiphenylbenzylguanidine, $NHPh \cdot NH \cdot C(NPh) \cdot NPh \cdot CH_2Ph$, formed by the action of sodium hydroxide on the benzyl chloride additive compound, crystallises in nodular aggregates of needles, melts at 153°, and is oxidised on exposure to the air, with formation of the red *azo*-compound.

3-*Anilino*-1 : 4-*diphenyl-5-methyl*-4 : 5-*dihydro*-1 : 2 : 4-*triazole*,

$C_2N_3HMePh_2\cdot NHPh$,

formed from triphenylaminoguanidine and acetaldehyde, crystallises from alcohol in glistening, white leaflets, melts at 131°, is readily soluble in chloroform, ether, or benzene, and on oxidation yields 1 : 4-*diphenyl-5-methyl*-3 : 5-endo*anilo*-4 : 5-*dihydro*-1 : 2 : 4-*triazole*,



which is formed also by boiling triphenylaminoguanidine with acetyl chloride in a reflux apparatus. It crystallises in moss-like aggregates of yellow needles, melts at 245—246°, is moderately soluble in methyl alcohol, acetone, or chloroform, forms easily soluble salts, and is decomposed by alcoholic alkali hydroxides, forming acetic acid and triphenylaminoguanidine. The *platinichloride*, $(C_{21}H_{18}N_4)_2,H_2PtCl_6$, forms microcrystalline leaflets and melts at 180—181°.

1 : 4-*Diphenyl-5-ethyl*-3 : 5-endo*anilo*-4 : 5-*dihydro*-1 : 2 : 4-*triazole*,

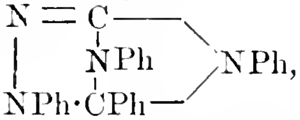
$C_{22}H_{20}N_4$,

formed by heating triphenylaminoguanidine with propionic chloride at 120° and finally at 140°, crystallises from dilute alcohol in long, brown, rectangular plates, melts at 229—230°, is moderately soluble in boiling benzene or chloroform, and readily so in dilute sulphuric or acetic acids.

3-*Anilino*-1 : 4 : 5-*triphenyl*-4 : 5-*dihydro*-1 : 2 : 4-*triazole*,

$C_2N_3HPh_3\cdot NHPh$,

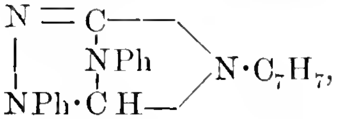
formed from triphenylaminoguanidine and benzaldehyde, crystallises from alcohol in colourless needles, melts at 165°, is readily soluble in chloroform, ether, or benzene, yields an odour of benzaldehyde, and when oxidised with sodium nitrite in acetic acid solution yields 1 : 4 : 5-*triphenyl*-3 : 5-endo*anilo*-4 : 5-*dihydro*-1 : 2 : 4-*triazole*,



which is formed also by heating triphenylaminoguanidine with benzoic chloride at 130° or by boiling the guanidine with benzoic acid and phosphorus pentachloride. It crystallises from alcohol in glistening, dark yellow, flat needles, melts at 231—232°, and forms an *additive* compound with benzoic chloride, $C_{33}H_{25}ON_4Cl$, which crystallises from ether in colourless needles, melts and decomposes with formation of benzoic chloride at about 262°, and when dissolved in alcohol yields triphenyl*endo*anilodihydrotriazole hydrochloride and ethyl benzoate, or benzamide when treated with alcoholic ammonia. The *nitrate*, $C_{26}H_{20}N_4,HNO_3$, crystallises from boiling water in colourless needles and melts above 270°; the *hydrochloride* forms sheaves of colourless, flat needles and melts at 270°. The *methiodide*, $C_{26}H_{20}N_4,MeI$, crystallises from its ethereal-alcoholic solution in colourless needles, melts at 231°, and is readily soluble in alcohol or chloroform.

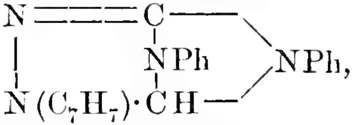
5-*Hydroxy-3-methylanilino*-1 : 4 : 5-*triphenyl*-4 : 5-*dihydro*-1 : 2 : 4-*triazole*, $OH\cdot C_2N_3Ph_3\cdot NMePh$, formed by the action of potassium hydroxide on the methiodide in ice-cooled absolute alcoholic solution, crystallises from a mixture of light petroleum and chloroform in yellow, hexagonal leaflets, melts at 158°, is readily soluble in chloroform, and when treated with dilute hydrochloric acid yields the *methochloride*, $C_{27}H_{23}N_4Cl$, which crystallises in spherical aggregates of white needles and melts above 265°.

Anilinophenyl-p-*tolylguanidine*, $NHPh\cdot NH\cdot C(NPh)\cdot NH\cdot C_7H_7$, formed from phenylhydrazine and carbodiphenylimide, crystallises in spherical aggregates of needles, melts at 184—185°, and condenses with formaldehyde to form 3-*anilino*-1-*phenyl*-4-p-*tolyl*-4 : 5-*dihydro*-1 : 2 : 4-*triazole*, $C_{21}H_{20}N_4$, which crystallises in colourless needles and melts at 148°. On oxidation with sodium nitrite, it yields a 1-*phenyl*-4-p-*tolyl*-3 : 5-endo*anilo*-4 : 5-*dihydro*-1 : 2 : 4-*triazole*,



which crystallises from a mixture of chloroform and light petroleum in dark yellow needles and melts at 210°.

3-*Anilino*-4-*phenyl*-1-p-*tolyl*-4 : 5-*dihydro*-1 : 2 : 4-*triazole*, $C_{21}H_{20}N_4$, formed from formaldehyde and *p*-toluidinodiphenylguanidine, crystallises from alcohol in glistening leaflets, melts at 123°, is easily soluble in benzene or chloroform, and on oxidation with nitrous acid yields 4-*phenyl*-1-p-*tolyl*-3 : 5-endo*anilo*-4 : 5-*dihydro*-1 : 2 : 4-*triazole*,



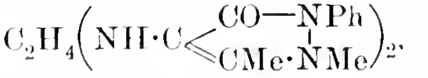
which crystallises in matted, glistening, light yellow needles and melts at 222°.

3-*Toluidino*-1-*phenyl*-4-p-*tolyl*-4 : 5-*dihydro*-1 : 2 : 4-*triazole*, $C_{22}H_{22}N_4$, formed from formaldehyde and anilinoditolylguanidine, crystallises in matted, long, white needles, melts at 132°, and on oxidation yields 1-*phenyl*-4-p-*tolyl*-3 : 5-endo*toluido*-4 : 5-*dihydro*-1 : 2 : 4-*triazole*, $C_{22}H_{20}N_4$, which forms glistening, yellow needles, melts at 170°, and is readily soluble in chloroform.

It has been found that as a test for nitrates nitron is even more delicate than was stated previously (Abstr., 1905, ii, 282).

G. Y.

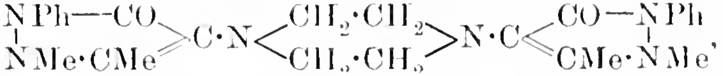
Synthetical Bases from 4-Aminoantipyrine. MAX LUFT (*Ber.*, 1905, **38**, 4044—4049. Compare Knorr and Stolz, Abstr., 1897, i, 112).—*Diantipyrylethylenediamine*,



$$C_2H_4\left(NH\cdot C\Big<\begin{matrix}CO-NPh\\ |\\ CMe\cdot NMe\end{matrix}\right)_2,$$

is formed when 2 mols. of 4-aminoantipyrine are heated with 1 mol. of ethylene dibromide in alcoholic solution on the water-bath, and 20 per cent. aqueous sodium hydroxide is added until the mixture is alkaline. It separates from a mixture of chloroform and ether as a colourless, flocculent powder, melts at 54°, is extremely hygroscopic, absorbs carbon dioxide from the atmosphere, and is precipitated unchanged on addition of alkali hydroxides to its acid solutions. The *platinichloride*, $C_{24}H_{28}O_2N_6H_2,PtCl_6$, forms orange needles and decomposes at 206—208°; the *picrate* crystallises in yellow needles and melts at 182°; the *mercurichloride* is insoluble in water and decomposes at 70—72°.

Diantipyryldiethylenediamine (1 : 4-*diantipyrylpiperazine*),



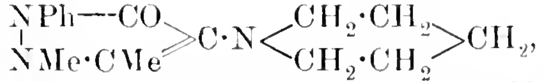
$$\begin{array}{l}NPh\text{—}CO\\ \mid\\ NMe\cdot CMe\end{array}\!\!>\!C\cdot N\!<\!\begin{array}{l}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{array}\!\!>\!N\cdot C\!<\!\begin{array}{l}CO\text{—}NPh\\ \qquad\;\mid\\ CMe\cdot NMe\end{array},$$

formed by the action of an excess of ethylene dibromide on antipyrine or on diantipyrylethylenediamine at 120—130°, crystallises from alcohol in colourless, nacreous, rhombic plates or needles, melts at 262°, is only sparingly soluble or is insoluble in all solvents, and is very stable towards alkali hydroxides. The *hydrochloride*,

$$C_{26}H_{30}O_2N_6,2HCl,$$

crystallises in colourless needles and melts at 248°; the *hydrobromide* melts at 237°; the *platinichloride*, $C_{26}H_{30}O_2N_6,H_2PtCl_6$, forms yellow needles, becomes grey at 100°, and decomposes at about 145°; the *mercurichloride* melts at 231°.

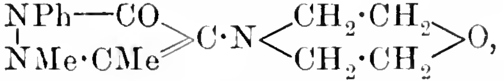
1-*Antipyrylpiperidine*,



$$\begin{array}{l}NPh\text{—}CO\\ \mid\\ NMe\cdot CMe\end{array}\!\!>\!C\cdot N\!<\!\begin{array}{l}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{array}\!\!>\!CH_2,$$

formed by heating 4-aminoantipyrine with αε-dibromopentane at 100°, crystallises from ether in colourless needles, has an odour of piperidine, melts at 144°, is soluble in alcohol, ether, benzene, or dilute acids, and is stable towards alkali hydroxides. The *hydrochloride* is deliquescent; the *hydriodide*, $C_{16}H_{21}ON_3,HI$, crystallises in glistening, yellow needles and decomposes with evolution of a gas at 215°; the *picrate* forms glistening, yellow prisms and melts and decomposes at 198°; the *platinichloride*, $C_{32}H_{42}O_2N_6,H_2PtCl_6$, forms plates and melts and decomposes at 208—210°; the *mercurichloride* crystallises in white, rhombic plates and melts and decomposes at 204°; the *methiodide* is obtained as a brown oil which solidifies to a yellow mass; it melts at 206° and decomposes when warmed with water.

1-*Antipyryltetrahydro*-1 : 4-*oxazine* (*antipyrylmorpholine*),



$$\begin{array}{l}NPh\text{—}CO\\ \mid\\ NMe\cdot CMe\end{array}\!\!>\!C\cdot N\!<\!\begin{array}{l}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{array}\!\!>\!O,$$

is obtained by digestion of 4-aminoantipyrine with ethylene oxide or ethylene bromohydrin in aqueous solution in a sealed tube for two days at the laboratory temperature, and then for fourteen hours at 60°, and heating the yellow, oily product with 50 per cent. sulphuric acid at 125—135° under pressure. The intermediately formed hydroxyethyl- and dihydroxyethyl-aminoantipyrine could not be isolated. The morpholine derivative crystallises in rosettes of long, colourless needles, has an aromatic odour, melts at 157°, and is soluble in alcohol, ether, benzene, or dilute acids. The *picrate*,

$$C_{15}H_{19}O_2N_3,C_6H_3O_7N_3,$$

crystallises in yellow plates and melts at 172°; the white, crystalline *mercurichloride* melts and decomposes at 201°; the *methiodide*, $C_{15}H_{19}O_2N_3,MeI$, crystallises in colourless needles, melts at 134°, and decomposes when warmed with water.

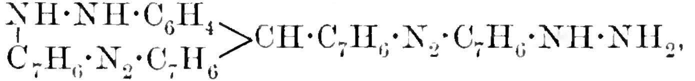
G. Y.

Action of Sulphur Dioxide on *m*-Toluenediazonium Chloride and Benzenediazonium Sulphate. JULIUS TRÖGER, W. HILLE, and P. VASTERLING (*J. pr. Chem.*, 1905, [ii], 72, 511—535. Compare Abstr., 1904, i, 118).—The red sulphonic acid formed by the action of sulphur dioxide on diazotised *m*-toluidine is considered now to have the constitution $C_7H_7\cdot N_2\cdot C_7H_6\cdot NH\cdot NH\cdot SO_3H$. It yields sulphuric acid when hydrolysed with aqueous hydrochloric acid and potassium sulphite with dilute potassium hydroxide, whilst reduction with stannous chloride and hydrochloric acid leads to the formation of sulphuric acid, ammonia, *m*-toluidine, and a tolylenediamine. The potassium salt is oxidised by mercuric oxide in aqueous solution with formation of the *potassium* salt, $C_7H_7\cdot N_2\cdot C_7H_6\cdot N_2\cdot SO_3K$, which does not give a red coloration on acidification and is reduced to the original sulphonate by ammonium sulphide. The colourless *sulphonic acid*, $C_{14}H_{14}O_3N_4S$, forms stable *silver*, *barium*, and *calcium* salts, whereas the red sulphonic acid reduces warm ammoniacal silver solutions.

The action of nitrous acid on the red sulphonic acid leads to the formation of a *derivative*, $C_7H_7\cdot N_2\cdot C_7H_6\cdot N_3$ (?), which forms short, dark red prisms or small, orange-red crystals and melts at 65°. The sulphonic acid condenses with salicylaldehyde in presence of sulphuric acid to form the *sulphate*,

$$OH\cdot C_6H_4\cdot CH(C_7H_6\cdot N_2\cdot C_7H_6\cdot NH\cdot NH_2)_2,H_2SO_4,$$

which is obtained in microscopic needles having a green sheen and dissolves in water to form a violet-blue solution. The *hydrochloride*, $C_{35}H_{36}ON_8,HCl$, and the *nitrate*, $C_{35}H_{36}ON_8,HNO_3$, formed by condensation of the sulphonic acid with salicylaldehyde in presence of hydrochloric and nitric acids respectively, have similar properties. The action of ammonia on the salts of the condensation product leads to the formation of an orange-red, crystalline *substance*,



$$\left.\begin{array}{l} NH\cdot NH\cdot C_6H_4 \\ | \\ C_7H_6\cdot N_2\cdot C_7H_6 \end{array}\right> CH\cdot C_7H_6\cdot N_2\cdot C_7H_6\cdot NH\cdot NH_2,$$

which melts at 130° and forms dark-coloured, crystalline salts with strong acids. The red sulphonic acid forms similar condensation *products* with other fatty and aromatic aldehydes and with ketones.

When a current of sulphur dioxide is passed through a cooled aqueous solution of benzenediazonium sulphate for one day, the *sulphonic acid*, $N_2Ph\cdot C_6H_4\cdot NH\cdot NH\cdot SO_3H$, is formed as a voluminous, red mass (compare Koenigs, Abstr., 1878, 219). It crystallises in microscopic, dark red needles, decomposes when dried at 100°, and when reduced with stannous chloride and hydrochloric acid yields sulphuric acid, ammonia, aniline, and *p*-phenylenediamine. When treated with sulphuric acid and sodium nitrite in alcoholic solution, it forms the *substance* $N_2Ph\cdot C_6H_4\cdot N_3$, which crystallises in small, bronze leaflets and melts at 90—91°. The *potassium* salt, $C_{12}H_{11}O_3N_4SK$, forms reddish-yellow crystals, dissolves in water forming a yellow solution which becomes red on addition of mineral acids, but not of carbon dioxide or hydrogen sulphide, and when oxidised with mercuric oxide yields the *potassium* salt, $N_2Ph\cdot C_6H_4\cdot N_2\cdot SO_3K$, from which it is again formed by reduction with ammonium sulphide. The colourless *sulphonic* acid, $C_{12}H_{10}O_3N_4S$, forms stable *barium*, *calcium*, and *silver* salts. G. Y.

Azo-dye from 3 : 4-Dichloroaniline. Badische Anilin- & Soda-fabrik (D.R.-P. 160788).—The diazonium compound of 3 : 4-dichloroaniline combines with sodium β-naphthol-3 : 6-disulphonate to yield a red azo-dye, which forms sparingly soluble metallic lakes remarkably stable towards light. The lakes of the corresponding azo-compounds from 2 : 4- and 2 : 5-dichloroanilines are so unstable towards light as to be practically useless. C. H. D.

Yellow Disazo-dyes. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 160674 and 160675).—The tetra-azotised solutions of benzidine-2 : 2′-disulphonic and 3 : 3′-tolidine-2 : 2′-disulphonic acids combine with 2 mols. of 1-phenyl-3-methyl-5-pyrazolone to form yellow *disazo-compounds* which dye wool. Similar dyes are obtained when the same tetrazo-compounds are combined with 2 mols. of methylindole or with 1 mol. of methylindole and 1 mol. of 1-phenyl-3-methyl-5-pyrazolone. C. H. D.

***o*-Hydroxyazo-dyes.** Badische Anilin- & Soda-fabrik (D.R.-P. 160536. Compare Abstr., 1905, i, 250).—The formation of diazosulphonates in the treatment of diazotised α- and β-naphthylaminedi- or poly-sulphonic acids with alkali acetates or carbonates is avoided by adding chlorine or alkali hypochlorites as well as the salt used to fix the acid, thus destroying any sulphites formed. Thus, a diazotised solution of β-naphthylamine-1 : 5-disulphonate is neutralised with sodium carbonate and an alkaline solution of sodium hypochlorite added. The temperature may rise to 35°. Combination with β-naphthol then takes place in the usual manner. C. H. D.

Hydrolysis of Egg-albumin. A. Adensamer and Ph. Hoernes (*Monatsh.*, 1905, **26**, 1217—1230. Compare Skraup, Abstr., 1904, i, 954).—Using Skraup's method, the authors have isolated from the products of the hydrolysis of egg-albumin, *d*-alanine, leucine, aminovaleric acid, and a mixture of substances which crystallises in microscopic plates or needles, melts in a sealed capillary tube at 280°, has $[\alpha]_D + 30{\cdot}196°$, and contains probably aminovaleric acid and *iso*leucine; it forms a copper salt which is readily soluble in methyl alcohol.

The copper salts obtained from the filtrate from the phosphotungstates were fractionally crystallised and made alkaline. The liberated ammonia was removed by distillation in a vacuum and the residue shaken with naphthalene-β-sulphonic chloride, when the only product obtained was naphthalene-β-sulphonamide.

No glycine, pyrrolidine-2-carboxylic, caseanic, or caseic acids could be detected amongst the products of hydrolysis, and if present they must be so only in extremely small quantities. G. Y.

Colloidal Solutions. The Globulins. William B. Hardy (*J. Physiol.*, 1905, **33**, 251—337. Compare Abstr., 1903, ii, 469).—This paper deals with the behaviour of globulins to acids, alkalis, and salts, and the properties of the solutions considered as cases of colloidal solution. Globulins are amphoteric electrolytes; the globulin salts ionise in solution, therefore in an electric field the entire mass of proteid

moves. A method for the direct measurement of the specific velocity of globulin ions is described. Among the many other points raised, for which the original paper must be consulted, the complete absence of "ionic" globulin from blood serum is noted. It is probable that the globulin is formed in serum by the decomposition of a more complex proteid.
W. D. H.

Globulins. J. Mellanby (*J. Physiol.*, 1905, **33**, 335—373).—Solution of globulin by a neutral salt is due to forces exerted by its free ions. Ions with equal valencies, whether positive or negative, are equally efficient, and the efficiencies of ions of different valencies are directly proportional to the squares of their valencies. The amount of globulin dissolved by a given percentage of neutral salt is directly proportional to the strength of the original globulin suspension. The precipitation of globulin by neutral salts depends on a molecular combination between the salt and globulin, the compound so formed being stable only in excess of the combining salt. Precipitation by salts of the heavy metals depends on the formation of a stable compound. Solution of globulin by acids or alkalis is of the nature of chemical combination. The relative solvent efficiencies of acids or alkalis are of the same order as their chemical avidities.
W. D. H.

The Group of Organic Acids containing Nitrogen and Sulphur which is present in Normal Human Urine. Stanislaus Bondzyński, St. Dombrowski, and Kazimierz Panek (*Zeit. physiol. Chem.*, 1905, **46**, 83—124. Compare Abstr., 1898, i, 501; 1902, i, 847).—*allo*Oxyproteic acid is precipitated by the addition of lead acetate, and the excess of lead removed by means of sodium carbonate. The addition of mercuric acetate and acetic acid precipitates a new acid, anti*oxyproteic acid*, in the form of its *mercuric* salt, and when the filtrate from this is neutralised with sodium carbonate a precipitate of the mercury salt of oxyproteic acid is obtained. The *barium* and *silver* salts of the new acid have been analysed, and the values calculated therefrom for the acid are C 43·21, H 4·91, N 24·4, S 0·61, and O 26·33 per cent. It gives a precipitate with phosphotungstic acid which is soluble in an excess or in water, and from this precipitate the barium salt may be obtained without precipitation with mercuric acetate. The *sodium* and *potassium* salts dissolve readily in water and yield emulsions with alcohol. The alkali-earth salts also dissolve readily in water, but are precipitated as white powders on the addition of alcohol. The acid is dextrorotatory. It gives neither the biuret nor the Millon reaction, but gives both Ehrlich's and Friedenwald's diazo-reactions.

To obtain a good yield of oxyproteic acid, it is advisable to remove the acetic acid and acetates before precipitating *anti*oxy- and oxy-proteic acids with mercuric acetate; if, however, the pure *anti*oxyproteic acid is required, the removal of the acetates is not recommended, as when these are absent a considerable quantity of the oxyproteic acid is precipitated with the antioxy-acid. Oxyproteic acid has the composition C 39·62, H 5·64, N 18·08, S 1·12, and O 35·54 per cent.

The acid previously described as *allo*oxyproteic acid was not pure, as acids free from sulphur and nitrogen are removed when the colourless mercuric salt is decomposed with hydrogen sulphide and extracted with ether. The composition of the pure *allo*-acid is C 41·33, H 5·70, N 13·55, S 2·19, and O 37·23 per cent. The salts are less soluble in alcohol than those of the other oxyproteic acids. These salts are often coloured by a substance which is comparatively rich in sulphur, and appears to be identical with urochrome.

Thiele's uroferric acid (Abstr., 1904, i, 452) closely resembles, but does not appear to be identical with, *allo*oxyproteic acid. J. J. S.

Action of Lactic Acid on Casein and Paracasein. O. LAXA (*Milchw. Zentr.*, 1905, 1, 538—547).—Casein combines with lactic acid to form a number of lactates. The latter are soluble in water, except those which contain less than 1 per cent. of lactic acid. By dialysis, a lactate containing from 1·4 to 1·9 per cent. of lactic acid is produced, whilst by "salting out" a solution of casein in lactic acid, a lactate with 7·5 per cent. of acid is obtained. To term the insoluble lactates "mono-lactates" and the soluble lactates "di-lactates" is therefore inconclusive. The casein lactates contain a proportionately small percentage of phosphorus, from 0·45 to 0·48 per cent. The lactic acid produced by bacteria in the milk converts the phosphates present into acid phosphates and at the same time combines with the casein, forming soluble and insoluble lactates. The soluble lactates, however, are precipitated subsequently by the mineral salts present, and the whole milk curdles. Impregnation of casein with calcium lactate renders the former exceedingly plastic. Paracasein is very probably a compound of casein with calcium phosphates. Acids convert it into casein and it yields the same lactates as casein.

W. P. S.

Amount of Glycine and Alanine from Casein. ZDENKO H. SKRAUP (*Monatsh.*, 1905, 26, 1343—1349. Compare Abstr., 1905, i, 619).—Details are given of the method by which *d*-alanine and glycine have been obtained from casein.

It is considered that the composition of casein varies, and that the appearance of glycine amongst the products of the hydrolysis of commercial casein purified by Hammarsten's method is not due to the presence of an impurity. G. Y.

Kyrines. ZDENKO H. SKRAUP and RUDOLF ZWERGER (*Monatsh.*, 1905, 26, 1403—1414. Compare Skraup, Abstr., 1905, i, 398; Siegfried, Abstr., 1903, i, 586; 1905, i, 104).—When casein is heated on the water-bath for one hour with an equal weight of concentrated hydrochloric acid, the mixture dissolves completely in an equal volume of water, and if the resulting solution is further heated its lævo-rotatory power changes to dextro-rotatory, becoming constant in about forty-eight hours; at the same time, the behaviour of the solution to phosphotungstic acid changes, the precipitates formed at first are resinous, but those obtained after about forty-two hours' heating on the water-bath consist of short prisms and contain nitrogen and carbon in the atomic proportion 1 : 2·6, which was found by Siegfried for his caseinokyrine. The basic syrup obtained on treatment of the crystalline phosphotungstate with baryta forms a double salt with cadmium iodide, containing nitrogen and carbon in the atomic proportion 1 : 2·6, a double salt with potassium iodide, containing nitrogen and carbon in the atomic proportion 1 : 2·4, and a derivative with naphthalene-β-sulphonic chloride, in which the proportion is 1 : 2·2. The basic syrup (30 grams) yields 21 grams of lysine picrate, 0·5 gram of arginine nitrate, and 1·5 grams of crude histidine, from which 0·2 gram of the crystalline hydrochloride is obtained. G. Y.

Gelatin. II. Zdenko H. Skraup and F. Heckel (*Monatsh.*, 1905, **26**, 1351—1358. Compare Abstr., 1905, i, 398, 619).—Gelatin was hydrolysed by heating with hydrochloric acid and the product evaporated in a vacuum and esterified by treatment with absolute alcohol and hydrogen chloride. After removal of ethyl aminoacetate hydrochloride, the filtrate was extracted with ether and the residual solution precipitated with phosphotungstic acid in three fractions. The final filtrate, after removal of the phosphotungstic acid, yielded a small amount of glutamic acid. The second phosphotungstate precipitate yielded lysine and arginine. The third precipitate was crystallised from water, when three fractions were obtained; the least soluble part yielded an uncrystallisable syrup; the moderately soluble fraction yielded a mixture of *d*-alanine and glycine, whilst the most soluble part yielded almost pure glycine.

d-Alanine and glycine are separated by repeated fractional crystallisation, alternately, of the copper salts and of the acids. G. Y.

Jecorin. J. Meinertz (*Zeit. physiol. Chem.*, 1905, **46**, 376—382).—Manasse states that Drechsel's jecorin yields on decomposition the same products as lecithin, with dextrose in addition. Bing regards it as a mixture of various compounds of lecithin, of which lecithin-dextrose is an abundant one. In the present research, jecorin was prepared from liver by Drechsel's method, treated with dilute hydrochloric acid, and dialysed; the dialysable substances are the reducing substance, a nitrogenous material, and inorganic matter containing calcium and phosphoric acid; the residue was without reducing action and showed all the properties of lecithin. W. D. H.

The Chromogen of the so-called Scatole-red contained in Normal Human Urine. J. Ph. Staal (*Zeit. physiol. Chem.*, 1905, **46**, 236—262).—Normal human urine, when mixed with hydrochloric acid and a few drops of potassium nitrite solution, yields, in addition to indigo-red, a dye which is insoluble in chloroform and differs spectroscopically from indigo red. A close examination of this dye proves it to be identical with Nencki and Sieber's urorosein (Abstr., 1883, 101). The chromogen which gives rise to this dye may be extracted by Stokvis' method (*Med. Tijdsch. Gen.*, 1901, i, 961). The ethyl acetate extract may be freed from indican by shaking with water, and when mixed with magnesium carbonate yields a *magnesium* derivative, which may be isolated by removing the ethyl acetate and extracting the residue with 90 per cent. alcohol. It is a brownish-yellow, amorphous powder, soluble in water, alcohol, acids, or alkalis, but insoluble in ether, chloroform, or acetone. With hydrochloric acid and a few drops of potassium nitrite solution, it yields the stable red dye, which may be extracted with amyl alcohol.

The composition of the magnesium compound is Mg 10·26, C 46·59, H 4·98, and N 3·35 per cent. It is not a "coupled" sulphuric or glycuronic acid, and is not a scatole derivative, as this base is not formed when the compound is reduced, distilled, or fermented by bacteria. When heated with sulphuric acid, it yields acetic and hippuric acids.
J. J. S.

Preparation and Analysis of Nucleic Acids. XI. Nucleic Acid from the Mammary Glands of the Cow. John A. Mandel and Phoebus A. Levene (*Zeit. physiol. Chem.*, 1905, **46**, 155—158. Compare Abstr., 1900, i, 572; 1901, i, 299, 623; 1902, i, 668, 779; 1904, i, 126; 1905, i, 105, 847).—The copper salt of the nucleic acid gave the following analytical data: C = 31·34, H = 4·07, N = 14·65, P = 8·48, Cu = 7·00 per cent. When hydrolysed with 2 per cent. sulphuric acid, 100 grams yield guanine 1·05 and adenine picrate 4·56 grams. With 25 per cent. sulphuric acid, thymine, 5 grams, and cytosine picrate, 10 grams, are obtained.

When distilled with hydrochloric acid, the acid yields furfuraldehyde, and with concentrated sulphuric acid, lævulic acid.
J. J. S.

Nucleic Acids of the Thymus. III. Hermann Steudel (*Zeit. physiol. Chem.*, 1905, **46**, 332—336. Compare Abstr., 1904, i, 837).—When hydrolysed with acids, nucleic acid yields both purine and pyrimidine bases among other substances. The relationship between these is doubtful. If a reducing agent is added to the acid used in hydrolysis, much of the purine bases is destroyed, but there is no corresponding increase in the pyrimidine bases. If the hydrolysis is carried out with sulphuric acid so energetically as to destroy all the purine bases, the same negative result regarding pyrimidine bases is obtained. Cytosine and thymine are present, but in smaller amount than in experiments where the hydrolysis was not carried so far.
W. D. H.

Catalysis and Enzyme Action. C. Hugh Neilson (*Amer. J. Physiol.*, 1906, **15**, 148—152).—Further evidence is adduced which shows the similarity between the action of enzymes and that of metallic catalysts. Platinum black and manganese dioxide act in the same way on salicin and amygdalin as emulsin does.
W. D. H.

Physico-chemical Nature and Activity of Enzymes. Luigi Marino and G. Sericano (*Gazzetta*, 1905, **35**, ii, 407—417).—The authors have prepared carefully purified specimens of emulsin and maltase, which were white and dissolved in water giving solutions having a faint reddish-yellow or brownish-red colour, according to the concentration. If a drop of a very concentrated solution of emulsin is added to a very large quantity of water, the latter becomes milky, but as more emulsin is added the amount remaining in solution gradually increases. The authors compare this phenomenon with that observed with readily hydrolysable inorganic salts. The deposited emulsin has the same composition as that in solution, and exhibits similar behaviour. At temperatures above about 30°, the emulsin solutions remain clear, however great the quantity of added water may be. Maltase exhibits similar comportment, but the temperature above which its solutions remain clear on dilution with water is lower than with emulsin.

Emulsin has the following percentage composition: carbon, 43·68; hydrogen, 7·62; and nitrogen, 13·64, that of maltase being: carbon, 43·48; hydrogen, 6·87; and nitrogen, 6·80.

On exposing an 18—20 per cent. emulsin solution to the action of sunlight in absence of oxygen, it was found that the activity of the enzyme decreased and increased in a periodic manner. The following are the relative amounts of salicin decomposed by a constant quantity of the emulsin solution after exposure to sunlight for different periods: at first, 93·6; after six days, 70·2; after eleven days, 15·1; after sixteen days, 28·0; after twenty-one days, 35·0; after twenty-six days, 38·5; and after sixty days, less than 10·6. After such exposure to sunlight, the emulsin has the same chemical composition and the same physical properties as the original enzyme. Emulsin solutions exposed to only the heat rays or only the light rays of the sunlight underwent no change. The weak sunlight of the end of October exerts no influence on the activity of emulsin solutions.

Maltase exhibits the same behaviour as emulsin when its solutions are acted on by sunlight. Solutions of emulsin and maltase of equal concentration have the same refractive index, specific rotatory power, and specific conductivity. T. H. P.

Studies on Enzyme Action. Lipase. HENRY E. ARMSTRONG (*Proc. Roy. Soc.*, 1905, *B* **76**, 606—608).—In the experiments on castor oil, ground castor oil seed was employed; in the experiments on other esters, the oil was first removed by means of ether.

The observations of Connstein and his co-workers, that ricinus lipase is effective only in presence of acid, and that it acts preferentially on the natural fats, are confirmed. Ethyl mandelate is not much affected by ricinus lipase, whereas it is readily attacked by animal lipase (compare Dakin, Abstr., 1904, i, 1071).

Attempts to prepare an extract containing an enzyme were unsuccessful. When the material, free from fat, is digested with the amount of sulphuric acid in presence of which hydrolysis of fatty oil is rapidly effected, the enzyme is destroyed. G. S.

Nuclease. FRITZ SACHS (*Zeit. physiol. Chem.*, 1905, **46**, 337—353).—The experiments recorded support the theory that ferments exist which are capable of cleaving nuclein with the liberation of nuclein bases. Such ferments are found in the extracts of many tissues, but especial attention is directed in the present research to the nuclease of the pancreatic juice; this is not identical with trypsin, but is destroyed by tryptic action. W. D. H.

Papain-digestion. Friedrich Kutscher and Lohmann (*Zeit. physiol. Chem.*, 1905, **46**, 383—386).—Contrary to Mendel's statement (Abstr., 1901, i, 355), it is found that abundant quantities of crystalline cleavage products are obtained by the action of papain on proteids. They resemble those obtained by the use of trypsin. Tetra- and penta-methylenediamines, which are characteristic of the prolonged action of pepsin, could not be prepared. W. D. H.

Action of Rennin. I. H. Reichel and Karl Spiro (*Beitr. chem. Physiol. Path.*, 1905, **7**, 485—507).—The experiments relate mainly to reaction velocity and show that within quite wide limits the amount of enzyme and the time of curdling are inversely proportional. The influence of calcium salts follows an equally simple law. The effect of other substances was also studied. W. D. H.

Ferment Action and Ferment Loss. II. H. Reichel and Karl Spiro (*Beitr. chem. Physiol. Path.*, 1905, **7**, 479—484. Compare Abstr., 1904, i, 1071).—In milk, the loss of the enzyme rennin is related to the amount of calcium salts present. In specimens containing such salts, the loss increases, and in those in which the calcium percentage is kept constant the amount lost rises with higher concentrations of rennin, and is relatively greater than in those poor in calcium salts. Magnesium chloride acts in a similar way, but not so markedly. Potassium thiocyanate increases the loss slightly; glycerol and urea increase it greatly, but possibly in some cases an injurious effect on the ferment has here to be dealt with, and not merely a division of the amount of ferment between curd and whey.

W. D. H.

Studies on Enzyme Action. VII. The Synthetic Action of Acids contrasted with that of Enzymes. Synthesis of Maltose and *iso*Maltose. E. Frankland Armstrong (*Proc. Roy. Soc.*, 1905, *B* **76**, 592—599. Compare Trans., 1903, **83**, 1305; Abstr., 1904, i, 956—958, 1070; 1905, i, 746).—When dextrose is condensed by means of hydrochloric acid (compare Fischer, Abstr., 1891, 412; 1896, 119), both maltose and its isomeride *iso*maltose are produced. To detect *iso*maltose, the acid was removed by means of lead carbonate and the filtered solution fermented with *Saccharomyces intermedians* to get rid of unaltered dextrose; from the resulting solution, an osazone was obtained which behaved in all respects like the osazone of *iso*maltose obtained by E. Fischer. In testing for maltose, the dextrose was removed from another portion of the solution by fermenting with *S. Marxiana*, which contains no maltase, and the maltose confirmed by observing the rotatory power of the solution, by preparation of the osazone, and by its behaviour towards maltase.

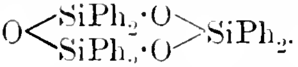
Dextrose was also condensed by means of maltase and emulsin. In the former case, *iso*maltose was produced, but the solution was not tested for maltose; with emulsin, maltose was formed, but probably not *iso*maltose. The investigation of these points is being continued.

The theory of condensation by acids and enzymes is discussed.

With acids, both isomerides are to be expected, since the condensation is "uncontrolled," but with enzymes, owing to their selective action, the process is probably controlled. Experiment shows, as in the above examples, that an enzyme favours the production of a sugar isomeric with that which it can hydrolyse; the question as to how the control of the enzyme is exerted so as to produce this result is considered. G. S.

Studies on Enzyme Action. VIII. The Mechanism of Fermentation. E. FRANKLAND ARMSTRONG (*Proc. Roy. Soc.*, 1905, *B* **76**, 600—605. Compare preceding abstract).—The action of twenty typical pure yeasts, prepared by Hansen's methods, on dextrose, mannose, lævulose, and galactose has been investigated. Whereas the three first-mentioned sugars were fermented, apparently with equal readiness, by all the yeasts, about half of the latter had no action on galactose, a result which is in accordance with previous observations. This inability to ferment galactose has nothing to do with the absence of hydrolysing enzymes, since it was observed with yeasts containing invertase, maltase, and lactase respectively. Further, dextrose, mannose, and lævulose were readily fermented by yeasts which do not contain any enzyme capable of inducing the hydrolysis of bioses. From these results, it is clear that the processes of enzymo-hydrolysis and of fermentation differ in some essential respects, although, for reasons given in a previous paper (Abstr., 1904, i, 957), it is probable that they are cognate phenomena.

It is pointed out that the three hexoses which behave alike have a common enolic form and the change to this is probably the initial stage in fermentation. The mechanism of the fermentation of galactose seems to be different from that of the other three sugars. G. S.

Diphenylsilicone and Benzylsilicon Compounds. WALTHER DILTHEY [and FRITZ EDUARDOFF] (*Ber.*, 1905, **38**, 4132—4136. Compare Abstr., 1904, i, 132, 464).—The gelatinous diphenylsilicone (diphenyl silicoketone) becomes crystalline when rubbed with a few drops of acetic anhydride. It separates from chloroform and light petroleum in clear, flat prisms melting at 188° and readily soluble in ether, benzene, or chloroform. Both the gelatinous and the crystalline compounds are trimolecular, probably  $O<\begin{matrix}SiPh_2\cdot O\\ SiPh_2\cdot O\end{matrix}>SiPh_2$.

Dibenzylsilicol, $Si(CH_2Ph)_2(OH)_2$, crystallises from a mixture of benzene and light petroleum, melts at 76°, and dissolves readily in ether, benzene, or chloroform. The yield is small. *Tribenzylsilicol*, $Si(CH_2Ph)_3\cdot OH$, is obtained when a larger quantity of magnesium benzyl chloride is used; it crystallises from alcohol in long, colourless needles and melts at 106°. J. J. S.

Organic Chemistry.

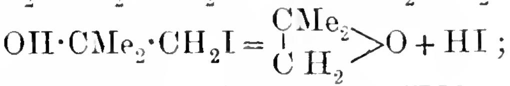
New Isomeride of Heptane: *s*-Tetramethylpropane [βδ-Dimethylpentane]. Michael I. Konowaloff (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 910—911).—For βδ-dimethylpentane (compare Chonin, Abstr., 1905, i, 729), the author gives the following constants: boiling point, 83—84° under 749 mm. pressure; sp. gr. 0·7022 at 0°/0° and 0·6879 at 22°/0°; n_D 1·38477 at 22°. T. H. P.

New Method of Preparing Olefines. Alphonse Mailhe (*Chem. Zeit.*, 1906, **30**, 37).—When the monohalogen substituted paraffins are passed through a glass tube containing reduced nickel, cobalt, or copper heated at 250° or more, they are decomposed into the corresponding halogen acid and an olefine; these two substances are prevented from recombining by passing through potassium hydroxide solution. The chloro-derivatives are decomposed below 250°, whilst the bromo- and iodo-derivatives require increasingly higher temperatures; ethyl iodide, for example, is only decomposed at a temperature of 360°. The dried chlorides of the bivalent metals nickel, cobalt, cadmium, iron, lead, barium, &c., also act catalytically in the same way at about 300°, barium chloride being most efficient. In the case of the bromo-derivatives, a slightly higher temperature, about 320°, is necessary, and, owing to the greater tendency of the decomposition products to reunite, the yield of hydrocarbon is not so good. The anhydrous bromides of lead, cadmium, nickel, or barium and the iodides of lead or cadmium have been found to act in a similar manner at 320°. Since the halogen derivatives of univalent metals are not able to effect this decomposition, it is assumed that the reaction entails the intermediate formation of an organo-metallic compound as follows:

$$MCl_2 + C_nH_{2n+1}Cl = HCl + ClM{\cdot}C_nH_{2n}Cl\,;$$
$$ClM{\cdot}C_nH_{2n}Cl = C_nH_{2n} + MCl_2.$$

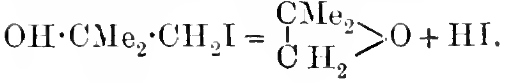
P. H.

Reaction of Iodine with *iso*Butylene. S. A. Pogorželsky (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 814—818. Compare Abstr., 1905, i, 165, 315).—The action of *iso*butylene on iodine in potassium iodide solution yields mainly trimethylcarbinol and *iso*butylene α-oxide, together with a small quantity of *tert.*-butyl alcohol. The author regards the reaction as expressed by either: (1) $CMe_2{:}CH_2 + I_2 = CMe_2I{\cdot}CH_2I$; $CMe_2I{\cdot}CH_2I + H_2O = OH{\cdot}CMe_2{\cdot}CH_2I + HI$;



$$OH{\cdot}CMe_2{\cdot}CH_2I = \left.\begin{matrix}CMe_2\\ |\\ CH_2\end{matrix}\right> O + HI\,;$$

or (2) $I_2 + H_2O = HI + HIO$; $CMe_2{:}CH_2 + HIO = OH{\cdot}CMe_2{\cdot}CH_2I$;



$$OH{\cdot}CMe_2{\cdot}CH_2I = \left.\begin{matrix}CMe_2\\ |\\ CH_2\end{matrix}\right> O + HI.$$

T. H. P.

Combustion of Acetylene in Oxygen. Paul Mauricheau-Beaupré (*Compt. rend.*, 1906, **142**, 165—166).—In addition to carbon dioxide and water vapour, the gaseous products of the oxyacetylene blowpipe flame contain oxides of nitrogen and ozone (compare Berthelot, Abstr., 1900, ii, 475, 538); after removing the oxides of nitrogen by means of ferrous sulphate crystals moistened with concentrated potassium carbonate solution (compare Gautier, Abstr., 1898, ii, 537), the amount of carbon monoxide in the residual gaseous mixture was determined by the method of Albert-Lévy and Pecoul (Abstr., 1905, ii, 203) and found to be less than 1 in 100,000.

M. A. W.

The Simplest Hydrocarbon with Two Conjugated Systems of Double Bonds. $\alpha\gamma\epsilon$-Hexatriene. PIETER VAN ROMBURGH and W. VAN DORSSEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, **8**, 565—568. Compare this vol., i, 141).—When slowly heated at 165°, and then gradually to 200°, the diformate of *s*-divinyl glycol, or a mixture of the diformate with the glycol, evolves carbon dioxide and a small amount of carbon monoxide, and yields a distillate consisting of two layers, of which the upper layer is *$\alpha\gamma\epsilon$-hexatriene*,

$$CH_2{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CH_2.$$

This is a colourless, strongly refracting liquid, which boils at 78·5—80° (corr.) under 766 mm. pressure and has the sp. gr. 0·7565 at 10° and $n_D = 1{\cdot}49856$ at 10°; it is reduced by sodium and boiling absolute alcohol, and is oxidised slowly when exposed to the air. It forms a *dibromide* melting at 89—90°, and a *tetrabromide* melting at 115°.

G. Y.

Conditions under which the Metal-ammonium Compounds reduce Halogen Derivatives of the Fatty Hydrocarbons. Preparation of Olefines and Paraffins. E. CHABLAY (*Compt. rend.*, 1906, **142**, 93—95. Compare Abstr., 1905, i, 502; Lebeau, Abstr., 1905, i, 401, 512).—Ethylene dichloride reacts with sodammonium to form ethylene, sodium chloride, and ammonia, according to the equation $C_2H_4Cl_2 + 2NaNH_3 = 2NaCl + C_2H_4 + 2NH_3$, and similar results were obtained when the dibromides of propylene, pseudobutylene, *iso*butylene, or trimethylene replaced the ethylene dichloride in the above reaction. The dichloride of methylene, ethylidene, or propylidene or $\beta\beta$-dichloropropane yields the corresponding paraffin (methane, ethane, or propane) by the action of sodammonium. M. A. W.

Pyrogenic Behaviour of Tetrachloroethylene, Acetyl Chloride, Trichloroacetic Acid, and Bromoform. MATTHIAS JOIST and WALTHER LÖB (*Zeit. Elektrochem.*, 1905, **11**, 938—944).—Experiments made in the way described previously (Abstr., 1902, i, 3) show that tetrachloroethylene yields hexachlorobenzene and hexachloroethane. The decomposition of acetyl chloride is represented by the equation $2CH_3{\cdot}COCl = 2HCl + 2CO + C_2H_4$. Bromoform yields tetrabromoethylene and bromine, whilst in presence of water formic acid is also produced. The reactions are explained as before by the intermediate formation of CCl_2, CBr_2, and similar unsaturated substances.

Trichloroacetic acid is entirely broken up, thus: $2CCl_3{\cdot}CO_2H + H_2O = 3CO + CO_2 + 4HCl + Cl_2$. T. E.

Di*iso*butenyl Tetrabromide [αβεξ-Tetrabromo-βε-dimethylhexane]. S. A. Pogorželsky (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 809—814).—*Diisobutenyl tetrabromide*,

$$CH_2Br\cdot CBrMe\cdot CH_2\cdot CH_2\cdot CBrMe\cdot CH_2Br,$$

separates from ether in monoclinic crystals [$a : b : c = 1\cdot2412 : 1 : 1\cdot2318$; $\beta = 118^\circ 56\cdot5'$] melting at 100°. T. H. P.

Etherates of Haloid Compounds of Magnesium. II. Action of Anhydrous Alcohols on Etherates of Magnesium Bromide; Crystalline Alcoholates of Magnesium Bromide. Boris N. Menschutkin (Reprint from *Bull. St. Petersburg Polytechnic Inst.*, 1905, 3, 29 pp. Compare Abstr., 1904, i, 215).—The etherates of magnesium bromide and iodide react readily with organic compounds of various kinds, such as alcohols, acids, aldehydes, ketones, and ethers. On dissolving $MgBr_2,Et_2O$ in a slight excess of an alcohol, heat is developed and the ether is replaced by the alcohol forming a compound of the type $MgBr_2,6R\cdot OH$. These compounds are colourless, hygroscopic, and slightly soluble in water. Each of them can be crystallised from the alcohol it contains, the readiness of crystallisation falling off continuously as the molecular weight increases. The melting points of the compounds formed with methyl, ethyl, propyl, *iso*butyl, and *iso*amyl alcohols are given below, together with those of the corresponding alcohols:

MeOH	− 94°	$MgBr_2,6MeOH$	190°
EtOH	− 112	$MgBr_2,6EtOH$	108·5
PrOH	− 127	$MgBr_2,6PrOH$	52
$C_4H_9\cdot OH$	− 108	$MgBr_2,6C_4H_9\cdot OH$	80
$C_5H_{11}\cdot OH$	− 117·2	$MgBr_2,6C_5H_{11}\cdot OH$	46

The solubilities of the separate compounds in the corresponding alcohols at different temperatures are given in the form both of tables and curves. T. H. P.

Etherates of Haloid Compounds of Magnesium. III. Action of Anhydrous Alcohols on Etherates of Magnesium Iodide; Crystalline Alcoholates of Magnesium Iodide. Boris N. Menschutkin (Reprint from *Bull. St. Petersburg Polytechnic Inst.*, 1905, 3, 12 pp. Compare preceding abstract).—Crystalline alcoholates of magnesium iodide can be prepared by a method analogous to that employed for the corresponding magnesium bromide compounds (*loc. cit.*). The ethylate of magnesium iodide crystallises in six-sided plates, 8—9 mm. in length, and rapidly turns yellow in the air. The melting points of the compounds prepared by the author are as follows: $MgI_2,6MeOH$, above 210°; $MgI_2,6EtOH$, 146·5°; $MgI_2,6PrOH$, 65—70°; $MgI_2,6C_4H_9\cdot OH$ (*iso*), 95—100°; $MgI_2,6C_5H_{11}\cdot OH$ (*iso*) could not be obtained in a crystalline form. The solubilities of the methylate in methyl alcohol and that of the ethylate in ethyl alcohol have been determined at various temperatures. T. H. P.

Etherates of Haloid Compounds of Magnesium. IV. Action of Water on the Etherates; Solubility of Hydrates of Magnesium Bromide and Iodide in Water. Boris N. Menschutkin (Reprint from *Bull. St. Petersburg Polytechnic Inst.*, 1905, 4, 26 pp. Compare preceding abstracts).—The action of small quantities of water on etherates of magnesium bromide and iodide at moderately high temperatures (35—40°) yields etherates of hydroxyhaloid compounds of magnesium. With larger quantities of water, acting at the ordinary temperature, the hexahydrate of magnesium bromide and the octahydrate of magnesium iodide are obtained.

The etherate of magnesium hydroxybromide,

$$MgBr\cdot OH,MgBr_2.2Et_2O,$$

has already been prepared by Holroyd (*Proc.*, 1904, 20, 38). The *etherate* of *magnesium hydroxyiodide*, $MgI\cdot OH,2Et_2O$, is obtained as a hygroscopic, unstable, white powder.

Magnesium bromide hexahydrate melts at 164° and its solubility in water has been determined from −5° to 164°. The solubility of magnesium iodide octahydrate, melting at 43·5°, has been measured from 0° to 43°, at which temperature it is converted into the hexahydrate, decomposing at above 200°; the solubility curve for the hexahydrate is given for the range of temperature 43—200°.

The solubility curves of hexahydrated magnesium bromide and iodide in water and of the crystalline methyl and ethyl alcoholates of magnesium bromide and iodide in methyl and ethyl alcohols are, in general, of the same type. The curve for $MgBr_2,6MeOH$ in methyl alcohol, however, although similar to the other curves, does not lie between that for $MgBr_2,6H_2O$ in water and that for $MgBr_2,6EtOH$ in ethyl alcohol; this depends on the divergence in character of methyl alcohol from its homologues. T. H. P.

Etherates of Haloid Compounds of Magnesium. V. Action of Esters: Compounds of Magnesium Iodide and Bromide with Esters. Boris N. Menschutkin (Reprint from *Bull. St. Petersburg Polytechnic Inst.*, 1905, 4, 37 pp. Compare preceding abstracts and Abstr., 1904, i, 215).—With many esters, magnesium iodide and bromide form compounds, which in many cases crystallise well.

The compounds of magnesium iodide with acetic esters, which are well-crystallised substances, melt at the following temperatures:

$MgI_2,6Me\cdot CO_2Me$, 121°.
$MgI_2,6Me\cdot CO_2Et$, 78·5°.
$MgI_2,6Me\cdot CO_2Pr^a$, 65°.
$MgI_2,6Me\cdot CO_2\cdot C_4H_9$ (*iso*), 87·5°.
$MgI_2,6Me\cdot CO_2\cdot C_5H_{11}$ (*iso*), 60°.

The alternate fall and rise of the melting point here exhibited finds a very close parallel in the behaviour of the melting points of the corresponding esters of furandicarboxylic acid (see Yoder and Tollens, Abstr., 1902, i, 49. Compare also Arbusoff, Abstr., 1905, i, 316). Solubility curves and tables are given for each of the above magnesium iodide compounds in the particular ester it contains. These compounds are all very hygroscopic and are decomposed by water with liberation of the esters from which they are prepared.

The following compounds have also been prepared : $MgI_2,6H{\cdot}CO_2Et$, which melts at 70·5° and the solubility of which in ethyl formate has been determined from 0° to 70·5° ; $MgBr_2,2C_6H_5{\cdot}CO_2Et$, melting at about 110° ; $MgBr_2,2C_6H_5{\cdot}CO_2C_4H_9$, melting at about 130° ;

$$MgI_2,3C_6H_5{\cdot}CO_2Me,$$

melting at 115—117° ; $MgI_2,3C_6H_5{\cdot}CO_2Et$, melting at 105° ;

$$MgBr_2,2CH_2(CO_2Et)_2,$$

melting at 135° ; $MgI_2,4CH_2(CO_2Et)_2$, melting at 115° and decomposing and resolidifying at 120—125°. T. H. P.

The ⋮C(OH) Group of Tertiary Alcohols. LOUIS HENRY (*Compt. rend.*, 1906, **142**, 129—136).—A theoretical paper in which the author discusses the effect on the ⋮C(OH) group of a tertiary alcohol of introducing negative elements or groups such as Cl, CN, or CO as substituents into the molecule, in respect of its behaviour towards such reagents as hydrochloric acid and acetyl chloride.

M. A. W.

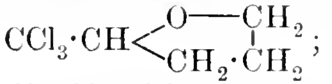
Application of Grignard's Reaction to Ethyl Chloroacetate. E. SÜSSKIND (*Ber.*, 1906, **39**, 225—226).—*Chloromethyldiethylcarbinol*, $CH_2Cl{\cdot}CEt_2{\cdot}OH$, obtained from magnesium ethyl bromide and ethyl chloroacetate, boils at 166—167° under the ordinary pressure and at 70—72° under 18 mm. By interaction with secondary amines, the following compounds have been obtained : *dimethylaminomethyldiethylcarbinol*, boiling at 172° under the ordinary pressure and at 62·5—63·5° under 12·5 mm., *diethylaminomethyldiethylcarbinol*, boiling at 89—90° under 20 mm. pressure, and *piperidinomethyldiethylcarbinol*, boiling at 112° under 15 mm. pressure. C. S.

εεε-Trichloro-α-methoxypentane-δ-ol and 2-Trichloromethyltetrahydrofuran. JULES HAMONET (*Compt. rend.*, 1906, **142**, 210—211. Compare Abstr., 1904, i, 467, 705 ; this vol., i, 58).—εεε-Trichloro-α-methoxypentane-δ-ol,

$$OMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CCl_3,$$

obtained by the action of chloral on the magnesium derivative of α-iodo-γ-methoxypropane, is a colourless solid melting at 59° and boiling at 142—143° under 17 mm. pressure ; it has an odour similar to that of camphor and a bitter taste, is insoluble in water, but readily soluble in alcohol, chloroform, or ether, crystallising from the last solvent in monoclinic plates [$a:b:c = 1{\cdot}008:1:1{\cdot}75$; $\beta = 108°25'$]. It does not reduce an alcoholic solution of silver nitrate in the presence of ammonia, but readily reduces Fehling's solution or silver oxide precipitated by an alkali.

An attempt to prepare the corresponding pentene derivative by distilling εεε-trichloro-α-methoxypropane-δ-ol with phosphoric oxide (compare Vitoria, Abstr., 1905, i, 110) was not successful, the product of the reaction being 2-*trichloromethyltetrahydrofuran*,



$$CCl_3{\cdot}CH{<}\begin{matrix}O\text{——}CH_2\\ CH_2{\cdot}CH_2\end{matrix} ;$$

it is a colourless, mobile liquid, with a strong odour similar to that of camphor, has a bitter and burning taste, and a sp. gr. 1·42 at 18° ; it boils at 90—91° under 17 mm. or 203—204° under 758 mm. pressure; it is insoluble in water, but soluble in alcohol or ether. It has no reducing action on alcoholic silver nitrate or on Fehling's solution, and is not readily attacked by alcoholic sodium hydroxide.

M. A. W.

Asymmetric Derivatives of Hexane-αζ-diol; Diethyl Ether and Di-iodo-derivative of Heptane-αη-diol. R. Dionneau (*Compt. rend.*, 1906, **142**, 91—92).—*ζ-Bromo-α-ethoxyhexane*, $OEt\cdot[CH_2]_6\cdot Br$, prepared by the action of hydrobromic acid on αζ-diethoxyhexane, has not yet been obtained quite pure, but forms the chief constituent of the fraction boiling between 121° and 123° under 35 mm. pressure. By boiling with sodium iodide in alcoholic solution, it is converted into *ζ-iodo-α-ethoxyhexane*, $OEt\cdot[CH_2]_6\cdot I$, a colourless liquid boiling at 138—139° under 35 mm. pressure, and having a sp. gr. 1·379 at 11°/4°. This forms a magnesium *derivative*, $OEt\cdot[CH_2]_6\cdot MgI$, which reacts with iodoethoxymethane to form *αη-diethoxyheptane*, $OEt\cdot[CH_2]_7\cdot OEt$ (compare Hamonet, Abstr., 1904, i, 467; 1905, i, 403), a colourless liquid with a fruity odour, boiling at 129° under 35 mm. pressure and having a sp. gr. 0·853 at 11°/4°. *αη-Di-iodoheptane*, $C_7H_{14}I_2$, prepared by the action of hydriodic acid in sealed tubes at 100° on the preceding compound, is a stable liquid which boils at 178° under 20 mm. pressure, has a sp. gr. 1·943 at 8°/8°, and solidifies to form colourless crystals melting at about 0°.

M. A. W.

αββ-Trichloroethyl Ether. Giuseppe Oddo and Efisio Mameli (*Atti R. Accad. Lincei*, 1905, [v], **14**, ii, 587—595. Compare Abstr., 1904, i, 280).—The action of 50 per cent. potassium hydroxide solution on αββ-trichloroethyl ether proceeds much more rapidly than that of water, but yields the same products; the same is the case with the action of an aqueous solution of ethylamine, and with that of saturated sodium hydrogen sulphite solution.

The action of dry ammonia on the ether yields dichloroacetal in quantities varying with the conditions, together with liquids boiling below and above 181—184° and complex resinous substances containing nitrogen.

When heated with magnesium, the ether is only slightly attacked, giving small quantities of substances boiling below and above 170—175°. Also when solvents are present, the magnesium effects but little action, yielding, when benzene is employed, dichloroacetal.

Zinc dust acts more readily on the ether than does magnesium, giving hydrogen chloride, dichloroacetaldehyde, and a voluminous, resinous mass. In presence of ethyl ether, an energetic reaction takes place on heating, but no organo-zinc compound analogous with the organo-magnesium compounds prepared by Grignard is obtained. On treating with water the product of the reaction between zinc and the trichloro-ether in presence of ethyl ether, it yields dichloroacetal, together with small quantities of dichloroacetaldehyde hydrate, of the additive product of dichloroacetaldehyde (1 mol.) with ethoxide (2 mols.), boiling at 110—111°, and of products boiling at above 184°.

Attempts have been made to prepare ββ-dichloroethyl ether by reducing the trichloro-ether with zinc or magnesium under various conditions, but without success.

Dichloromonothioacetal, $CHCl_2\cdot CH(OEt)\cdot SEt$, prepared by the interaction of ethyl mercaptan and *αββ*-trichloroethyl ether, was obtained as a yellowish-red liquid boiling at 110—125° under 20—30 mm. pressure.

Phenylethyldichloroacetal, $CHCl_2\cdot CH(OEt)\cdot OPh$, prepared by the action of anhydrous sodium phenoxide on *αββ*-trichloroethyl ether in benzene solution, is a reddish-brown, unstable liquid, which boils at 165—170° under 40 mm. pressure, dissolves in alcohol, decolorises potassium permanganate, and combines with bromine, giving a white, solid substance.

The interaction of molecular proportions of *αββ*-trichloroethyl ether and pyridine in ethereal solution yields an oily, red precipitate, which forms: (1) a *platinichloride*, $(CHCl_2\cdot CHCl\cdot OEt,C_5H_5N)_2,PtCl_4$, crystallising from dilute hydrochloric acid in mamillary masses of slender, orange-yellow needles melting and decomposing at 208—209°; (2) an *aurichloride*, $(CHCl_2\cdot CHCl\cdot OEt,C_5H_5N),AuCl_3$, as a heavy, yellow precipitate melting at 92—93°. T. H. P.

Liberation of Carbon Monoxide [from Organic Compounds].

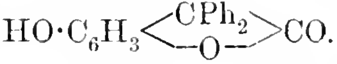
AUGUSTIN BISTRZYCKI and B. VON SIEMIRADZKI (*Ber.*, 1906, **39**, 51—66).—The following compounds yield carbon monoxide when heated alone or with sulphuric acid, sulphur chloride, phosphorus pentachloride, &c. Quantitative experiments were made on all substances the formulæ of which are given.

I. Formic acid and its methyl and ethyl esters.

II. *α*-Hydroxy-acids and their derivatives, namely, diphenyleneglycollic acid, $C_{14}H_{10}O_3$; lactic acid, $C_3H_6O_3$; *α*-methoxyphenylacetic acid, $OMe\cdot CHPh\cdot CO_2H$; mandelic acid, $C_8H_8O_3$; *o*-methoxyphenoxyacetic acid, $OMe\cdot C_6H_4\cdot O\cdot CH_2\cdot CO_2H$; phenylchloroacetic acid, and *α*-alanine, $C_3H_7O_2N$.

III. Oxalic acid and its derivatives: ethyl oxalate and oxamide, $C_2H_4O_2N_2$.

IV. *α*-Dicarbonyl compounds: pyruvic acid, $C_3H_4O_3$, and benzoylformic acid, $C_8H_6O_3$.

V. Tertiary acids: sulphocamphylic acid, $C_{10}H_{16}O_4$; *m*-chloro-*p*-hydroxytriphenylacetic acid, $C_{20}H_{15}O_3Cl$; camphoronic acid, $CO_2H\cdot CMe_2\cdot CMe(CO_2H)\cdot CH_2\cdot CO_2H$; dimethylmalonic acid, $C_5H_8O_4$; methyl diphenyl-*p*-tolylacetate, $C_{22}H_{20}O_2$; *p*-tolyldiphenylacetolactone, $C_{21}H_{16}O_3$; 3:5-(or 2:4-)dihydroxytritanolactone,  $HO\cdot C_6H_3{<}\overset{CPh_2}{\underset{O}{}}{>}CO$.

VI. Secondary and primary acids: *p*-hydroxydiphenylacetic acid, $C_{14}H_{12}O_3$; diphenylacetic acid, $C_{14}H_{12}O_2$; and (in small amounts) phenylacetic acid, $C_8H_8O_2$; palmitic acid, $C_{16}H_{32}O_2$.

VII. Ketones and aldehydes: benzaldehyde (small amounts); camphor at 360°; potassium lævulate (by electrolysis); *p*-tolylpentadecyl ketone.

m-*Chloro*-p-*hydroxytriphenylacetic acid*, $CO_2H \cdot CPh_2 \cdot C_6H_3Cl \cdot OH$, prepared by condensing benzilic acid with *o*-chlorophenol by means of stannic chloride, crystallises from a mixture of benzene and light petroleum in colourless, microscopic tablets and melts at 189°.

Methyl diphenyl-p-*tolylacetate* (compare Bistrzycki and Wehrbein, Abstr., 1901, i, 712) crystallises from methyl alcohol in long, colourless, microscopic tablets and melts at 135°. T. M. L.

The Capacity of Methoxyl and Ethoxyl Groups for Replacement by [Alkyl] Radicles. Synthesis of Polybasic Acids. SERGIUS N. REFORMATSKY (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 881—889).—In the replacement of alkoxyl groups by alkyl radicles by the action of, for instance, an organo-zinc compound on an ester, it is generally assumed that the carbonyl group reacts in the first stage of the change and the alkoxyl group in the second, thus: (1) $R \cdot CO \cdot OEt + ZnR'I = IZn \cdot O \cdot CRR' \cdot OEt$; (2) $IZn \cdot O \cdot CRR' \cdot OEt + ZnR'I = CRR'_2 \cdot OZnI + ZnI \cdot OEt$. It has not, however, been shown that the OEt group is not directly replaced by the alkyl radicle, forming $R \cdot CO \cdot R'$, which would then react with ZnR′I, giving

$$CRR'_2 \cdot OZnI.$$

The author's attempts to isolate intermediate products formed in reactions similar to the above have as yet yielded no definite results (see this vol., i, 138). T. H. P.

Double Acetates of Gold. Crystallised Barium Auryl Oxide. F. WEIGAND (*Zeit. angew. Chem.*, 1906, **19**, 139—140).—The double acetates of gold with calcium, barium, strontium, magnesium, or lead were prepared by adding the hydroxides of these metals to a solution of auric chloride and dissolving the moist precipitates so obtained in boiling glacial acetic acid; the solutions deposited monoclinic crystals of compounds of the following formulæ: $Ba(C_2H_3O_2)_2,2Au(C_2H_3O_2)_3$; $Sr(C_2H_3O_2)_2,2Au(C_2H_3O_2)_3,2H_2O$;

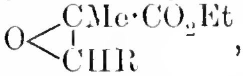
$$Ca(C_2H_3O_2)_2,2Au(C_2H_3O_2)_3,2H_2O ;$$

$Mg(C_2H_3O_2),2Au(C_2H_3O_2)_3,4H_2O$; $Pb(C_2H_3O_2)_2,2Au(C_2H_3O_2)_3,2H_2O$. These substances are all soluble in water to give neutral solutions which slowly decompose; when heated on platinum foil, the gold is partially volatilised in the form of red fumes. The filtrate from the precipitate obtained by adding barium hydroxide to the auric chloride solution deposited, after some time, small, yellowish-green, rhombic crystals having the composition $Ba(O \cdot AuO)_2,5H_2O$; these dissolve with difficulty in water to give an alkaline solution. P. H.

The Oxidation of Oils. HENRY R. PROCTER and W. E. HOLMES (*J. Soc. Chem. Ind.*, 1905, **24**, 1287—1290).—The results of numerous experiments are given in tabular form with the object of elucidating the chemical changes which take place when oils are oxidised by blowing air through them while in a heated condition. Without exception, the sp. gr. and refractive index increased as oxygen was absorbed and the iodine number diminished, but complete saturation was never reached. In some instances, the iodine number remained unaltered during the first three or four hours' blowing, although oxygen was being absorbed, indicating that the oxygen was not attached to the unsaturated linkings measured by the iodine number. When, however, the iodine number commenced to decrease, it did so rapidly. The oils experimented with comprised liver oils, fish oils, linseed oil, rape oil, cotton-seed oil, olive oil, castor oil, lard oil, &c.

W. P. S.

Pyruvic Acid. William Oechsner de Coninck (*Bull. Acad. roy. Belg.*, 1905, 524—525).—When pyruvic acid is dissolved in sulphuric acid and the solution gently heated, it blackens and carbon monoxide, mixed with a little carbon dioxide, is evolved. Concentrated nitric acid converts it into oxalic acid, but with dilute nitric acid, carbon dioxide and a little formic acid are formed. Pyruvic acid reduces chromic acid, auric chloride, and selenic acid when warmed with their aqueous solutions. At temperatures slightly higher, it reduces mercuric chloride to mercurous chloride and mercurous nitrate to metallic mercury. When warmed with mercuric or silver oxide, some acetic acid is produced. Pyruvic acid reduces uranic sulphate, uranium nitrate, and potassium dichromate. With the last-named, carbon dioxide and some acetic acid are produced. T. A. H.

Glycidic Condensation of Aldehydes with Ethyl α-Chloropropionate. Georges Darzens (*Compt. rend.*, 1906, **142**, 214—215. Compare this vol., i, 62).—Acetaldehyde, propaldehyde, or *iso*valeraldehyde condense with ethyl α-chloropropionate to form $\alpha\beta$-disubstituted glycidates of the type  $O<\begin{matrix}CMe\cdot CO_2Et\\ |\\ CHR\end{matrix}$, but the yield is poor, 20 to 30 per cent. of the theoretical. The aromatic aldehydes readily condense with ethyl α-chloropropionate, and the substituted glycidic acids thus prepared yield ketones of the type $R\cdot CH_2\cdot COMe$ on distillation; *ethyl β-phenyl-α-methylglycidate* boils at 153—154° under 18 mm. pressure, and the corresponding acid yields carbon dioxide and benzylmethyl ketone on distillation. *Ethyl β-anisyl-α-methylglycidate* boils at 189—190° under 20 mm. pressure, and the aqueous solution of the corresponding sodium salt is decomposed by boiling into sodium hydrogen carbonate and anisyl ketone. *Ethyl β-piperonyl-α-methylglycidate* boils at 205—210° under 25 mm. pressure, and piperonylacetone is obtained by boiling an aqueous solution of the corresponding sodium salt. *Ethyl β-furyl-α-methyl glycidate* is a colourless liquid boiling at 150—151° under 30 mm. pressure, and on boiling with sodium carbonate yields *furylacetone*,  $\begin{matrix}CH{-}{-}O\\ ||\\ CH\cdot CH\end{matrix}>C\cdot CH_2\cdot CO\cdot CH_3$; this is a colourless liquid with an odour of horse-radish, and boils at 179—180°; its *semicarbazone* melts at 173—174° and its *oxime* boils at 135—140° under 25 mm. pressure. M. A. W.

Dialkylmalonic Acids. Hans Meyer (*Ber.*, 1906, **39**, 198—200. Compare E. Fischer and Dilthey, Abstr., 1902, i, 269).—The dimethyl ester of dimethylmalonic acid is transformed into the amide,

$$CMe_2(CO\cdot NH_2)_2,$$

when kept at the ordinary temperature with concentrated ammonia for twenty-four hours and occasionally shaken. The corresponding diethyl ester is not transformed under similar conditions even after several weeks.

Dimethyl methylethylmalonate, $CMeEt(CO_2Me)_2$, is a colourless oil distilling at 189—191° (uncorr.) and *dimethyl diethylmalonate* distils at 204—205°. Dimethyl methylethylmalonate reacts with ammonia yielding *methylethylmalonamide*, $CMeEt(CO{\cdot}NH_2)_2$, which forms glistening crystals melting at 182—183°, and *methyl methylethylmalonamate*, $CO_2Me{\cdot}CMeEt{\cdot}CO{\cdot}NH_2$, which sublimes in glistening needles melting at 106—108°. Dimethyl- and diethyl-malonyl chlorides readily react with concentrated ammonium hydroxide yielding the corresponding diamides, whereas methylethylmalonyl chloride yields methylethylacetamide (Scheuble and Loebl, Abstr., 1904, i, 466). Fischer and Dilthey's views regarding the formation of the amides from the esters are adversely criticised. J. J. S.

Action of Ammonia on Itaconic and Pyrocinchonic Anhydrides.

Luciano Rossi (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1905, [iii], 11, 254—258. Compare Foà, Abstr., 1904, i, 230).—The action of alcoholic ammonia on pyrocinchonic anhydride at different temperatures always yields pyrocinchonimide, which, however, melts at 113° if obtained at low temperatures, or at 118° if at high temperatures.

The action of liquid ammonia on pyrocinchonic anhydride yields pyrocinchonimide at the ordinary temperature, whilst at higher temperatures (70—100°) a yellowish-brown syrup is obtained.

These results demonstrate, firstly, the great resistance exerted by the double linking of pyrocinchonic anhydride against the introduction of an amino-group, and, secondly, the great stability of the anhydride.

In the cold or at 70—80°, itaconic anhydride gives with liquid ammonia a yellowish-brown acid syrup which contains nitrogen, dissolves Peligot's copper oxide giving a green solution, and is probably a mono-amide. In the reaction at 100°, the yellowish-brown syrup obtained probably contains a small amount of amino-acid.

T. H. P.

Action of Zinc on a Mixture of Ethyl Orthoformate and Ethyl Bromopropionate. Synthesis of *s*-Trimethyl*iso*butanetricarboxylic Acid.

S. Sokolowsky (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 889—896).—Zinc acts on a mixture of ethyl orthoformate (1 mol.) and ethyl α-bromopropionate (3 mols.) according to the equations: (1) $CHMeBr{\cdot}CO_2Et + Zn = BrZn{\cdot}CHMe{\cdot}CO_2Et$; (2) $3BrZn{\cdot}CHMe{\cdot}CO_2Et + CH(OEt)_3 = CH(CHMe{\cdot}CO_2Et)_3 + 3ZnBr{\cdot}OEt$.

*Triethyl s-trimethyl*iso*butanetricarboxylate* [*γ-ethylpentane-$\beta\delta\alpha'$-tricarboxylate*], $C_{16}H_{28}O_6$, thus obtained, is a colourless, mobile liquid boiling at 200—201°. On hydrolysis, it yields the *monoethyl* ester,

$$CO_2Et{\cdot}CHMe{\cdot}CH(CHMe{\cdot}CO_2H)_2,$$

which crystallises from water in shining, white needles and from benzene in long, shining plates melting at 109° and is readily soluble in ether or chloroform. The *calcium*, $Ca(C_{12}H_{18}O_6),4H_2O$, *barium*, and *sodium* salts of the monoethyl ester were prepared and analysed.

T. H. P.

Formation of Ethyl Sodiodicarboxyglutaconate from Ethyl Malonate, Sodium Ethoxide, and Chloroform. CARL COUTELLE (*J. pr. Chem.*, 1906, [ii], **73**, 49—100. Compare Conrad and Guthzeit, Abstr., 1883, 311).—Recrystallised ethyl sodiocarboxyglutaconate is obtained by Conrad and Guthzeit's reaction (*loc. cit.*), in a yield of 41·36 per cent. of the theoretical, if the absolute alcoholic solution of 4 mols. of sodium ethoxide is cooled to the laboratory temperature, 2 mols. of ethyl malonate and 1¼ mols. of chloroform added, and the mixture quickly boiled in a reflux apparatus. Smaller yields are obtained by varying the proportions of the reacting substances, or the temperature or order of mixing. Only 0·55 gram of the sodio-ester was obtained by the action of sodium and chloroform on 16 grams of ethyl malonate in benzene solution (compare Oppenheim and Precht, this Journal, 1876, ii. 69). The formation of ethyl sodiodicarboxyglutaconate is not due to the action of primarily formed ethyl *o*-formate on ethyl malonate, as when boiled with ethyl *o*-formate and sodium in alcoholic solution in a reflux apparatus, 32 grams of ethyl malonate yielded only 1·1 grams of the sodio-ester (compare Claisen, Abstr., 1897, i, 592). The sodio-ester remains unchanged when boiled with chloroform in alcoholic solution.

The formation of carbon monoxide, which must result from the decomposition of ethyl *o*-formate primarily formed, is shown by passing a current of hydrogen successively through the reacting mixture and a solution of cuprous chloride (Hullemann, Abstr., 1890, 582). The salts which separate from the reaction mixture are sodium chloride, ethyl sodiomalonate, and sodium formate.

The reddish-brown residue obtained from the mother liquor, on distillation of the alcohol in a vacuum, was extracted successively with light petroleum, A, and with acetone, B. A. The light petroleum extract contains ethyl malonate and *ethyl* iso*butanehexacarboxylate*, $CH[CH(CO_2Et)_2]_3$; this is a viscid, yellow oil, which boils at 235° under 13 mm. pressure, has an odour of onions, dissolves in alcoholic sodium ethoxide to form a dark red solution, decolorises immediately dilute potassium permanganate solution in presence of sodium carbonate, interacts with bromine in carbon disulphide, evolving hydrogen bromide, and when boiled with 10 per cent. hydrochloric acid is hydrolysed with formation of carbon dioxide and iso*butanetricarboxylic acid*. This is obtained as a brownish-red resin; it forms a *barium* salt, $C_{14}H_{14}O_{12}Ba_3,4H_2O$, and the *trimethyl* ester,

$$CH(CH_2{\cdot}CO_2Me)_3,$$

which is a colourless liquid boiling at 180—185° under 23 mm. pressure.

Hydrolysis of the ethyl hexacarboxylate with alcoholic potassium hydroxide leads to the formation of a red *oil*, which deposits needles melting at 129°, or with baryta water to the formation of barium formate and malonate (compare Bottomley and Perkin, Trans., 1900, **77**, 294; Guthzeit and Engelmann, Abstr., 1902, i, 742). When heated with aniline at 150°, the ethyl hexacarboxylate forms malonanilide and the *penta-anilide*,

$$CO_2Et{\cdot}CH(CO{\cdot}NHPh){\cdot}CH[CH(CO{\cdot}NHPh)_2]_2,$$

which crystallises from much alcohol and melts at 245°.

B. The acetone solution contains the last traces of ethyl sodiodicarboxyglutaconate, sodium malonate, and sodium formate. On treatment with sulphuric acid and ether, sodium formate yields an ethereal solution, which, when shaken with water and mercuric oxide, filtered, and heated in the water-bath, gives a grey precipitate of metallic mercury. When treated in the same way, sodium malonate forms a yellow precipitate, whilst glutaconic acid and ethyl sodiodicarboxyglutaconate do not form precipitates. In a mixture of formates and malonates, the formic acid is detected by this reaction, the malonic acid by the formation of its sparingly soluble barium salt.

On evaporation of the acetone solution, treatment of the residue with chloroform, and evaporation of the extract, a red, resinous *mass* is obtained; this contains probably a *sodio*-derivative of ethyl *iso*butanehexacarboxylate.

In the quantitative examination of the products of the reaction, the formic acid is estimated by Lieben's method (see Scala, Abstr., 1891, 248), after precipitation of the malonic acid by means of barium chloride and alcohol, or after liberation of the formic acid by means of phosphoric acid and distillation in a current of steam, in which malonic acid is not volatile. As ethyl dicarboxyglutaconate is slightly volatile in a current of steam, the distillate is filtered after some hours, whereby a saturated solution of the ester is obtained; with mercuric chloride, 100 c.c. of this form 0·0551 gram of a precipitate, which weight is deducted from that of the mercuric chloride formed in the estimation of formic acid. As the barium derivative of ethyl dicarboxyglutaconate is only sparingly soluble in alcohol, it is precipitated partially together with the barium malonate; the amount of the latter which, when dried at 100°, has the composition $C_3H_2O_4Ba,5/6H_2O$ (compare Guthzeit and Bolam, Abstr., 1898, i, 12) is determined by indirect analysis.

Ethyl sodiodicarboxyglutaconate and ethyl *o*-formate could not be estimated directly.

Under the conditions most favourable to the formation of ethyl sodiocarboxyglutaconate, 100 grams of ethyl malonate, 29 grams of sodium as sodium ethoxide, and 38 grams of chloroform interact to form 50·3 grams of ethyl sodiodicarboxyglutaconate, 32·6 grams of sodium malonate, 10·06 grams of ethyl sodio*iso*butanehexacarboxylate, 3·99 grams of the free ethyl hexacarboxylate, 3·27 grams of sodium formate, 0·18 gram of carbon monoxide, and 0·66 gram of ethyl *o*-formate, more than 13 grams of the ethyl malonate remaining unchanged.

G. Y.

Formaldehyde and Formate Formation. HANS EULER and ASTRID EULER (*Ber.*, 1906, **39**, 36—39. Compare Abstr., 1905, i, 633).—More exact measurements have given for the dissociation-constant of formaldehyde acting as a weak acid the value $1{\cdot}4 \times 10^{-14}$ at 0°, in close agreement with the approximate value 1×10^{-14} previously obtained with formaldehyde containing methyl alcohol. T. M. L.

Aldehydes as Acids. HANS EULER (*Ber.*, 1906, **39**, 344—350. Compare Euler and Euler, Abstr., 1905, i, 633).—Acetaldehyde has the dissociation constant $K = 0{\cdot}8 \times 10^{-11}$ at 0°, as determined by the depression of the freezing point of the solution of its sodium salt (Goldschmidt and Röder, Abstr., 1895, i, 657), or $K=0{\cdot}5\times10^{-14}$ at 1°, as determined by the conductivity of its sodium salt solution; the mean constant is $K=0{\cdot}7\times10^{-14}$ at 0°. As ammonia forms complex compounds, which are not electrolytically dissociated, and not salts, with acetaldehyde, the conductivity of aqueous ammonia is diminished on addition of the aldehyde.

Chloral hydrate has the dissociation constant $K=1\times10^{-11}$ at 18°, as determined by the change in the conductivity of dilute ammonia which takes place on the addition of the aldehyde, or $K=0{\cdot}8\times10^{-11}$ at 18°, as calculated from the comparison of the conductivity of dilute solutions of its ammonium salt with the conductivities of similar solutions of the ammonium salts of boric acid and phenol.

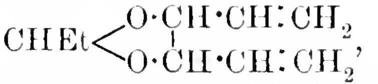
The salts of acetone with alkalis or with hydrogen chloride are dissociated hydrolytically to too great an extent to permit of the determination of the acid dissociation constant by either the conductivity or the cryoscopic method. Furfuraldehyde has only feeble salt-forming properties; its dissociation constant as an acid is 1/100 of that of acetaldehyde.

The acid dissociation constant of dextrose, $K=1{\cdot}8\times10^{-13}$ at 0°, as determined with the sodium salt by the cryoscopic method, agrees with that calculated by Madsen (Abstr., 1901, ii, 228) from the rate of hydrolysis of the ester.

As in dextrose and lævulose solutions containing the equivalent amount of sodium hydroxide the hexose is present chiefly in the form of the ion, the rotation of an alkaline hexose solution is due principally to that of the sodium salt.

With sodium light at 0°, *N*-dextrose solution, when mixed with equal volumes of water, *N*-sodium hydroxide, 2*N*-sodium hydroxide, 2*N*-potassium hydroxide, and *N*/2 sodium hydroxide has the rotations 10·4°, 8·1°, 7·8°, 7·8°, and 9·9° respectively, whilst *N*/2 dextrose solution with equal volumes of water, *N*/2 sodium hydroxide, and 2*N*-sodium hydroxide, has the rotations 5·2°, 4·2°, and 4·2° respectively. G. Y.

The Reduction of Acraldehyde and some Derivatives of *s*-Divinyl Glycol (γδ-Dihydroxy-αε-hexadiene). PIETER VAN ROMBURGH and W. VAN DORSSEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, **8**, 541—544. Compare Griner, Abstr., 1893, i, 237).—When reduced with zinc dust and glacial acetic acid, acraldehyde yields allyl and propyl alcohols, and the *substance*

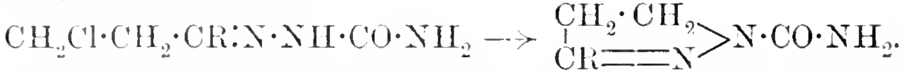


$$\mathrm{CHEt}\left\langle\begin{matrix}\mathrm{O{\cdot}CH{\cdot}CH{:}CH_2} \\ | \\ \mathrm{O{\cdot}CH{\cdot}CH{:}CH_2}\end{matrix}\right.,$$

which is formed also by heating propaldehyde with *s*-divinyl glycol at 90° for six days. It is a neutral liquid, which boils at 59·5—60° under 15 mm. pressure, is not decomposed by potassium hydroxide, sodium, or phosphorus pentachloride, and does not form a benzoyl derivative when treated with benzoyl chloride and pyridine; it yields an odour of aldehyde, and forms a brownish-black, resinous mass when treated with dilute acids, and forms an *additive compound* with bromine in carbon tetrachloride solution.

The *diformate*, formed by heating *s*-divinyl glycol with formic acid, is a colourless liquid which boils at 109° under 20 mm. pressure and has the sp. gr. 1·0747 at 11°. G. Y.

β-Chloroethyl Ketones and Alkyl Vinyl Ketones. Edmond E. Blaise and M. Maire (*Compt. rend.*, 1906, 142, 215—217).—β-Chloroethyl alkyl ketones of the type $CH_2Cl\cdot CH_2\cdot CO\cdot R$, readily obtained by the action of β-chloropropionyl chloride on the corresponding zinc alkyl, are liquids with a faint odour; their semicarbazones are unstable and readily converted into the carbamide of a pyrazole according to the equation



$$CH_2Cl\cdot CH_2\cdot CR{:}N\cdot NH\cdot CO\cdot NH_2 \longrightarrow \begin{array}{l} CH_2\cdot CH_2 \\ | \\ CR{=\!=\!=}N \end{array}\!\!>N\cdot CO\cdot NH_2.$$

Ethyl β-chloroethyl ketone boils at 68° under 20 mm. pressure. *β-Chloroethyl propyl ketone* boils at 73° under 10 mm. pressure. *β-Chloroethyl* iso*butyl ketone* boils at 80° under 12 mm. pressure.

When the alkyl β-chloroethyl ketones are boiled with diethylaniline, they yield the corresponding alkyl vinyl ketones,

$$CH_2Cl\cdot CH_2\cdot CO\cdot R \longrightarrow CH_2{:}CH\cdot CO\cdot R,$$

in the form of mobile liquids with an intensely penetrating odour; *ethyl vinyl ketone* boils at 31° under 47 mm. pressure; *propyl vinyl ketone* boils at 24° under 10 mm. pressure; and iso*butyl vinyl ketone* boils at 32° under 10 mm. pressure. These compounds polymerise rapidly under the action of heat or of alkalis, and yield semicarbazosemicarbazones with semicarbazide, hydroxylamino-oximes with hydroxylamine, pyrazoles with hydrazine, or phenylpyrazoles with phenylhydrazine; the last compounds give an intense violet-red colour with a trace of nitric acid. The pyrazoles are basic liquids forming salts, platinichlorides, picrates, and phenylcarbamides, and with secondary bases yielding additive compounds of the type $NEt_2\cdot CH_2\cdot CH_2\cdot CO\cdot R$, which are also basic and form picrates and platinichlorides. *Ethyl β-diethylaminoethyl ketone* boils at 80° under 10 mm. pressure, and *ethyl β-piperidinoethyl ketone* boils at 107° under 11 mm. pressure. M. A. W.

Formation of Sugar from Formaldehyde. Hans Euler and Astrid Euler (*Ber.*, 1906, 39, 39—45).—The action of alkalis on formaldehyde leads both to the formation of formates and the formation of sugars, but the latter process is not directly dependent on, and does not run parallel with, the former; addition of formate does not affect the rate at which sugar is formed. Curves are given to show the rate at which sodium carbonate is neutralised by formaldehyde previously to the formation of sugar. The concentration of formaldehyde at which sugar-formation sets in is dependent on the initial concentrations of the sodium carbonate and of the aldehyde, and sugar-formation never appears to occur until a part of the aldehyde has been converted into formate and alcohol; the most suitable concentration is nearly half an equivalent of soda for each equivalent of aldehyde. Experiments were also made with calcium carbonate as a condensing agent, the increased time required being compensated for by the increased stability of the sugar and the more constant composition of the solutions; it was noticed that sugar formation proceeds very slowly at first, but after boiling for several hours, proceeds very rapidly to a limit; this is explained by the formation of intermediate compounds, and the presence of glycollaldehyde was actually proved.

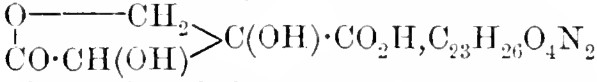
T. M. L.

Formation of *i*-Arabinoketose from Formaldehyde. Hans Euler and Astrid Euler (*Ber.*, 1906, 39, 45—51).—When formaldehyde is condensed by means of calcium carbonate, the chief product is a pentose, which was identified by means of its osazone and phenylmethylosazone, and by oxidation with bromine and with nitric acid as *i*-arabinoketose. A small amount of a hexose is also produced. If the action of the alkali is stopped before half the formaldehyde has disappeared, glycollaldehyde is one of the chief products, but glyceraldehyde could not be detected.

T. M. L.

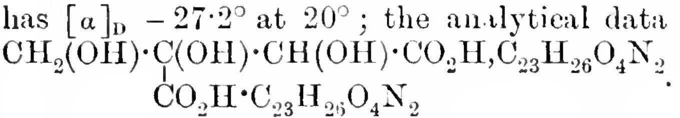
Apiose. Eduard Vongerichten and Fr. Müller (*Ber.*, 1906, 39, 235—240. Compare Abstr., 1901, i, 40, 646; 1902, i, 425).—Apiose obtained from the leaves of parsley is identical with that obtained from the seeds. *Apiose phenylbenzylhydrazone*, $C_{18}H_{22}O_4N_2$, separates from benzene solution in colourless, crystalline flocks which melt at 135°. By the action of formaldehyde, apiose is recovered as a colourless syrup, which in aqueous solution has $[\alpha]_D$ $+3{\cdot}8°$ at 20°, and is in all respects identical with the apiose from which the hydrazone was prepared.

At 50°, the oxidation of calcium apionate by three times its weight of nitric acid of sp. gr. 1·2 results in the formation of an *acid*, isomeric with trihydroxyglutaric acid, the *calcium* salt of which has $[\alpha]_D$ $+6{\cdot}58°$ at 20°. The oxidation of the acid by silver oxide produces glycollic acid. Neutralised with brucine, the acid yields two salts; the one insoluble in acetone corresponds with the formula



$$\begin{array}{l} O\text{———}CH_2 \\ | \\ CO{\cdot}CH(OH) \end{array}\!>C(OH){\cdot}CO_2H,C_{23}H_{26}O_4N_2,$$

has $[\alpha]_D$ $-23{\cdot}7°$ at 20°, and the lactonic acid obtained from it is converted on boiling with baryta water into the dibasic hydroxy-acid. The other *brucine* salt is soluble in acetone, melts at 148—150°, and has $[\alpha]_D$ $-27{\cdot}2°$ at 20°; the analytical data agree with the formula



$$\begin{array}{l} CH_2(OH){\cdot}C(OH){\cdot}CH(OH){\cdot}CO_2H,C_{23}H_{26}O_4N_2 \\ \qquad\quad\;| \\ \qquad\quad CO_2H{\cdot}C_{23}H_{26}O_4N_2 \end{array}.$$

Of the known trihydroxyglutaric acids, only the inactive ribotrihydroxyglutaric acid is capable of lactone-formation; it is quite different from the hydroxymethyltartaric acid described above.

C. S.

Action of Oxygen on Aliphatic Amines in Presence of Copper. Wilhelm Traube and Albert Schönewald (*Ber.*, 1906, 39, 178—184).—When an aqueous solution of ethylamine is shaken for several days with copper powder in the presence of oxygen at the ordinary temperature, a copious absorption of oxygen is observed (some 7 litres for 10 grams of ethylamine), the copper is oxidised to the hydroxide, and the ethylamine to acetaldehyde and ammonia. Nitrogen and nitrous acid do not appear to be formed.

When a 5 per cent. solution of aldehyde-ammonia is shaken with copper and oxygen, very little oxidation occurs. It is thus possible that the primary oxidation product in the earlier experiments was aldehyde-ammonia and not free aldehyde and free ammonia, since the latter would tend to become oxidised to nitrous acid.

Methylamine reacts in much the same manner as ethylamine, yielding formaldehyde and ammonia.

Sodium-glycine, copper, and oxygen yield considerable quantities of nitrous acid and probably glyoxylic acid. J. J. S.

Electro-synthesis in the Oximo-ether Group. Celso Ulpiani and G. A. Rodano (*Atti R. Accad. Lincei*, 1905, [v], **14**, ii, 601—607. Compare Abstr., 1905, i, 260).—Using platinum electrodes and a current intensity of 0·2—0·25 ampere, the authors have electrolysed the sodium or potassium derivative of ethyl oximinomalonate, ethyl α-oximinopropionate, and ethyl α-oximinobutyrate. These compounds, which have the general formula $CRR'{:}NONa$, are decomposed into metal, which evolves hydrogen at the negative pole, and the anion $CRR'{:}NO\cdot$; of the last, two groups combine at the positive pole.

In this way, the sodium hydrogen derivative of ethyl oximinomalonate, $OH\cdot N{:}C(CO_2Et)_2,ONa\cdot N{:}C(CO_2Et)_2$, yields the *compound*

$$NO\cdot C(CO_2Et)_2\cdot C(CO_2Et)_2\cdot NO$$

as an oil which is insoluble in alkali and yields Liebermann's reaction characteristic of true nitroso-compounds.

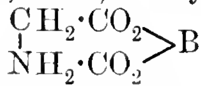
The potassium derivative of ethyl α-oximinopropionate,

$$OK\cdot N{:}CMe\cdot CO_2Et,$$

yields the *compound* $NO\cdot CMe(CO_2Et)\cdot CMe(CO_2Et)\cdot NO$ as an oil, which is insoluble in alkali and gives Liebermann's reaction.

The potassium derivative of ethyl α-oximinobutyrate yields the *compound* $CH_2Me\cdot C(NO)(CO_2Et)\cdot C(NO)(CO_2Et)\cdot CH_2Me$, which is an oil insoluble in alkali and giving Liebermann's reaction. T. H. P.

Isolation of Amino-acids. Max Siegfried (*Ber.*, 1906, **39**, 397—401. Compare Abstr., 1905, i, 59; ii, 332).—Glycine is readily precipitated as *barium carbaminoacetate*,



$$\begin{matrix}CH_2\cdot CO_2\\ | \\ NH_2\cdot CO_2\end{matrix}\!\!>Ba,$$

when carbon dioxide is led into a solution of the amino-acid in baryta water at 0° until phenolphthalein is decolorised and the mixture then kept for some time at 0°. Better yields are obtained when more baryta water is added after the carbon dioxide has been led in, and when the precipitate is washed with dilute barium hydroxide solution instead of with water.

Pure glycine is obtained when the barium salt is decomposed with ammonium carbonate solution, filtered, and the solution evaporated.

Glycylglycine yields a similar *barium* salt, $C_5H_6O_5N_2Ba$, which is much more readily soluble in water. It is most readily obtained by the addition of alcohol, and when decomposed with ammonium carbonate yields pure glycylglycine.

Lysine and albumoses give similar barium salts. Glycine and alanine can be separated with great readiness by this method, as the barium salt from alanine is readily soluble in water. J. J. S.

Synthesis of Polypeptides. XIV. EMIL FISCHER (*Ber.*, 1905, **39**, 453—474).—*a-Bromo*iso*hexoyldiglycylglycyl chloride*,

$$C_4H_9\cdot CHBr\cdot CO\cdot[NH\cdot CH_2\cdot CO]_2\cdot NH\cdot CH_2\cdot COCl,$$

prepared by the action of acetyl chloride and phosphorus pentachloride on bromo*iso*hexoyldiglycylglycine, freshly crystallised from alcohol, is obtained as a colourless powder easily decomposed by water. It reacts with glycine ethyl ester in chloroform solution to form *a-bromo*iso*hexoyltriglycylglycine ethyl ester*, crystallising in colourless, microscopic needles which become brown at 235° (corr.) and melt and evolve gas at 241° (corr.).

*a-Bromo*iso*hexoyltriglycylglycine*,

$$C_4H_9\cdot CHBr\cdot CO\cdot[NH\cdot CH_2\cdot CO]_3\cdot NH\cdot CH_2\cdot CO_2H,$$

prepared by the interaction of the above chloride with glycine, crystallises in microscopic, colourless plates, which become brown at 212° (corr.) and melt and decompose at 218° (corr.). *a-Bromo*iso*hexoyltetraglycylglycine*, $C_4H_9\cdot CHBr\cdot CO\cdot[NH\cdot CH_2\cdot CO]_4\cdot NH\cdot CH_2\cdot CO_2H$, formed by the interaction of the chloride with glycine anhydride, is obtained as a crystalline powder which turns brown at 230° (corr.) and melts at 237° (corr.).

Leucyltetraglycylglycine,

$$C_4H_9\cdot CH(NH_2)\cdot CO\cdot[NH\cdot CH_2\cdot CO]_4\cdot NH\cdot CH_2\cdot CO_2H,$$

prepared by the action of aqueous ammonia on the foregoing, forms a colourless, crystalline powder which on heating becomes coloured at 225° (corr.) and partially melts and decomposes at 240° (corr.). It shows a marked biuret coloration.

*a-Bromo*iso*hexoylpentaglycylglycine*, formed by the interaction of diglycylglycine with bromo*iso*hexoyldiglycylglycine chloride, crystallises in colourless aggregates of no definite crystalline form, which become coloured at 220° (corr.) and melt at 250° (corr.).

Leucylpentaglycylglycine,

$$C_4H_9\cdot CH(NH_2)\cdot CO\cdot[NH\cdot CH_2\cdot CO]_5\cdot NH\cdot CH_2\cdot CO_2H,$$

prepared by the action of aqueous ammonia on the foregoing, also has no definite crystalline structure, becomes yellow at 220°, and decomposes at 270°. It gives a strong biuret coloration.

A method for the preparation of *d*-alanine from silk is described at length. This crystallises from water in well-formed, centimetre long, rhombic crystals [$a:b:c = 0{\cdot}9784:1:0{\cdot}4924$]. *d*- and *l*-Alanine have the same taste. The hydrochloride has $[\alpha]_D + 10{\cdot}3°$ at 20°; the racemate can only be removed from the active substance by crystallisation of the free amino-acid. d-*Alanyl*-d-*alanine* crystallises in centimetre long, thin prisms, has $[\alpha]_D - 21{\cdot}6°$ at 20°, and melts and decomposes at about 298° (corr.), some 20° higher than the racemic alanylalanine. In hydrochloric acid solution, it has $[\alpha]_D$ about $-36{\cdot}5°$ at 20°; on heating with 10 per cent. acid, it is converted into alanine, about 73 per cent. being changed after five hours and 87 per cent. after seven and a half hours' heating.

d-*Alanine anhydride* (cis-*dimethyldiketopiperazine*) crystallises in silvery, glistening leaflets which melt at 297° (corr.) and have $[\alpha]_D$ − 28·8° at 20°; the inactive compound melts at 282°.

Diglycylglycine methyl ester,

$NH_2\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2Me$,

prepared by the action of methyl alcohol and hydrogen chloride on the tripeptide, crystallises in long needles grouped in stellar aggregates which melt indefinitely about 111° (corr.); the *hydrochloride* crystallises in glistening, small plates, sinters at 200°, and melts and decomposes at 204° (corr.).

Pentaglycylglycine methyl ester,

$NH_2\cdot CH_2\cdot CO\cdot[NH\cdot CH_2\cdot CO]_4\cdot NH\cdot CH_2\cdot CO_2Me$,

prepared by heating the powdered diglycylglycine methyl ester at 100°, when it condenses with elimination of methyl alcohol, when separated from hot water forms a fine precipitate having no definite crystalline form and decomposing between 200° and 300°.

Pentaglycylglycine, prepared by the action of sodium hydroxide on the foregoing, is obtained as a colourless powder very sparingly soluble in water, which begins to decompose above 256° (corr.) and gives the biuret coloration; the *nitrate* crystallises in microscopic needles melting and decomposing at about 240° (corr.).

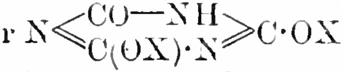
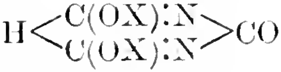
Along with the above, what is probably a still higher condensation product is obtained on heating diglycylglycine methyl ester: this gives a strong biuret reaction. E. F. A.

Amino- and Diazo-malonic Esters. Oscar Piloty and J. Neresheimer (*Ber.*, 1906, 39, 514—517).—*Ethyl aminomalonate hydrochloride*, $NH_2\cdot CH(CO_2Et)_2,HCl$, is obtained by passing dry hydrogen chloride into absolute alcohol containing sodium aminomalonate in suspension, or by reducing ethyl *iso*nitrosomalonate with aluminium amalgam. It crystallises from acetone in small, colourless needles and melts and decomposes at 162°. The *hydrochloride* of the corresponding *methyl* ester is easily soluble in water, and is precipitated from methyl-alcoholic solution by the addition of ether in small, colourless, rhombic crystals, frequently twinned, which melt and decompose at 159°. Each of the preceding ester hydrochlorides on treatment with ammonia yields aminomalonamide, the melting point of which is 192°, 10° higher than the value found by Conrad and Guthzeit (Abstr., 1882, 947). When a cold concentrated aqueous solution of ethyl aminomalonate hydrochloride is treated with nitrous acid and the product extracted with ether, an intensely yellow ethereal solution is obtained; after evaporation of the ether, a viscous, yellow oil remains, which is probably *ethyl diazomalonate*, since it has an odour resembling that of ethyl diazoacetate, explodes on heating, and is decomposed by mineral acids with violent evolution of nitrogen. C. S.

Cyanuric Acid as a Pseudo-acid. Arthur Hantzsch (*Ber.*, 1906, 39, 139—153. Compare Ponomareff, Abstr., 1886, 216).—Cyanuric acid is a tricarbimide, and as a complete pseudo-acid should be termed pseudocyanuric acid. The three pseudo-groups CO·NH can be transformed into the groups C(OH):N, which can then form salts. The transformation proceeds in three distinct stages; the first stage proceeds most readily and the last least readily. The first group is partially transformed by water alone, as the aqueous solution of cyanuric acid behaves as a feeble monobasic acid (at 25°, $K = 0{\cdot}000018$). Preparations of the acid from different sources all give the same result. The temperature-coefficient of the conductivity increases rapidly with the temperature, as is also the case with other pseudo-acids. The transformation of the first CO·NH group is complete in the presence of one equivalent of alkali, as the primary metallic cyanurates, $C_3N_3O_3H_2X$, are neutral to phenolphthalein. Thus, when titrated with $N/10$ sodium hydroxide in the presence of phenolphthalein, cyanuric acid acts as a monobasic acid.

These primary cyanurates have the same properties, whether prepared from concentrated or dilute, from hot or cold solutions. The following are described: *Ammonium* salt, $C_3N_3O_3H_2NH_4,H_2O$; this readily loses ammonia on exposure to the air, and at 130° leaves a residue of pure cyanuric acid. *Calcium* salt, $(C_3N_3O_3H_2)_2Ca,8H_2O$, slender needles only sparingly soluble in hot water; it retains part of its water even at 200°. *Magnesium* salt, $(C_3N_3O_3H_2)_2Mg,14H_2O$, needles readily soluble in hot water; when heated it decomposes before it is completely dehydrated. The same salt is obtained when the secondary sodium salt is treated with magnesia mixture.

The second CO·NH group is only partially transformed into $C(OX){:}N$ when treated with two equivalents of alkali in aqueous solution; solutions of the composition $C_3N_3O_3H_3,2NaOH$ are strongly hydrolysed. The transformation is, however, complete at the ordinary temperature when the secondary salt is insoluble, for example, calcium, barium, and silver salts. The following secondary salts are described: *Sodium* salt, $C_3N_3O_3HNa_2,H_2O$, which is precipitated even when a large excess of alkali is present. It crystallises in needles and may be dehydrated at 130°; its aqueous solution is strongly alkaline and hydrolysed to an appreciable extent, even more strongly than disodium hydrogen phosphate, as is shown by conductivity determinations. *Calcium* salt, $C_3N_3O_3HCa,3H_2O$, is precipitated at 0° or at the ordinary temperature, and may be dehydrated at 165°. At 100°, it becomes converted into the monohydrate, $C_3N_3O_3HCa,H_2O$, which is also formed when the salt is precipitated from boiling solutions or from the trisodium salt at 0°. It also may be dehydrated at 165°. The conversion of the monohydrate into the trihydrate has not been accomplished. *Barium* salts, $C_3N_3O_3HBa,3H_2O$ and $C_3N_3O_3HBa,H_2O$. The trihydrate cannot be transformed into the monohydrate by heating in a thermostat. *Silver* salt, $C_3N_3O_3HAg_2,H_2O$, is precipitated from both the mono- and di-sodium salts. The anhydrous salt may be obtained by heating the monohydrate or by precipitating the salt at 100°.

The third CO·NH group is not transformed at the ordinary temperature when a large excess of alkali is present, even when the tertiary salts are insoluble. At the ordinary temperature, cyanuric acid is a dibasic acid only. The secondary salts are all pseudo-acids, either  $N\Big<\begin{matrix}CO-NH\\ C(OX)\cdot N\end{matrix}\Big>C\cdot OX$ or  $NH\Big<\begin{matrix}C(OX){:}N\\ C(OX){:}N\end{matrix}\Big>CO$. The third CO·NH group is transformed at 100°, and tertiary salts can then be obtained.

The tertiary sodium salt, $C_3N_3O_3Na_3,H_2O$, is precipitated in slender needles when a cold solution of the acid in excess of 20 per cent. sodium hydroxide is heated to 100°. It cannot be recrystallised on account of the readiness with which it is hydrolysed and decomposed by carbon dioxide; it appears to be stable in presence of its mother liquor. It may also be precipitated by the addition of alcohol to a solution of the acid in sodium hydroxide (three equivalents). Two equivalents of alkali in its solution may be titrated by standard acid, using phenolphthalein as indicator. The conductivity of its aqueous solution has a high value due to considerable hydrolysis, and in this respect is identical with the solution of the acid in sodium hydroxide (three equivalents). The tertiary *calcium*, *barium*, and *silver* salts are all anhydrous, and are only precipitated at 100°; at the ordinary temperature, secondary salts are usually obtained. In the preparation of the tertiary salts, pure sodium hydroxide must be employed, and the solutions must be protected from atmospheric carbon dioxide.

When the silver salt is treated with sodium hydroxide solution, the secondary silver salt and silver oxide are formed.

The tertiary *mercuric* salt may be obtained at 0° or at the ordinary temperature.

When cyanuric acid is evaporated with mercuric chloride solution, the double *compound*, $2C_3N_3O_3H_3,HgCl_2,4H_2O$, is obtained in the form of lustrous plates which effloresce on exposure to the air.

Aluminium salts could not be prepared. J. J. S.

Acetylenic Amides and Nitriles. CHARLES MOUREU and I. LAZENNEC (*Compt. rend.*, 1906, **142**, 211—214).—Acetylenic amides of the type $R\cdot C{\vdots}C\cdot CO\cdot NH_2$ are readily prepared by the action of ammonia on the corresponding ester. Amylpropiolamide,

$$CH_3\cdot[CH_2]_4\cdot C{\vdots}C\cdot CO\cdot NH_2$$

(compare Abstr., 1903, i, 312), melts at 91°; *hexylpropiolamide*, $CH_3\cdot[CH_2]_5\cdot C{\vdots}C\cdot CO\cdot NH_2$, melts at 92°, and phenylpropiolamide melts at 106° (compare Stockhauser and Gattermann, Abstr., 1893, i, 163); they crystallise in colourless plates, are readily soluble in alcohol, methyl alcohol, or chloroform, less soluble in ether, and sparingly so in water; phenylpropiolamide is converted into benzoylacetamide by the action of sulphuric acid and water (compare Obrégia, Abstr., 1892, 324).

The acetylenic nitriles $R\cdot C{\vdots}C\cdot CN$ are obtained by the action of phosphoric oxide on the corresponding amide. *Amylpropiolonitrile*, $CH_3\cdot[CH_2]_4\cdot C{\vdots}C\cdot CN$, boils at 194—196° (corr.) under 760 mm. or 80—81° under 13 mm. pressure, has a sp. gr. 0·8508 at 13°/4°, and n_D 1·4553 at 13°; *hexylpropiolonitrile*, $CH_3\cdot[CH_2]_5\cdot C{\vdots}C\cdot CN$, boils at 212—213° (corr.) under normal, or 95—96° under 13 mm. pressure, has a sp. gr. 0·8493 at 14·4°/4° and n_D 1·45637 at 14·4°; phenylpropiolonitrile, $CPh{\vdots}C\cdot CN$, melts at 41°, boils at 228—229° (corr.) under normal, or at 105—106° under 13 mm. pressure, has a sp. gr. 1·0046 at 41·5°/4°, and n_D 1·58535 at 41·5° (compare *Bull. Soc. chim.*, 1902, [iii], **26**, 99; Claisen, Abstr., 1904, i, 14). By the action of alcoholic potassium hydroxide, the acetylenic nitriles yield the corresponding acid and compounds of the type $R\cdot C(OEt){:}CH\cdot CN$, and by the action of sulphuric acid the nitriles of the aliphatic series yield the corresponding acid, whilst phenylpropiolonitrile yields benzoylacetamide. M. A. W.

Action of Potassium Cyanide on Sodium Tetrathionate and Dithionate. August Gutmann (*Ber.*, 1906, **39**, 509—513).—The reaction between sodium tetrathionate and potassium cyanide in the presence of alkali was quantitatively examined and shown to follow a course represented by the equation: $Na_2S_4O_6 + 2CNK + 2NaOH = 2CNSK + Na_2SO_4 + Na_2SO_3 + H_2O$. Potassium cyanate and potassium sulphite do not react either at the ordinary temperature or on warming. Sodium dithionate is stable towards potassium cyanide even at 100°. C. S.

Detection and Precipitation of the Ferrous Iron in Aqueous Solutions of Potassium Ferrocyanide. Fritz Haber (*Zeit. Elektrochem.*, 1905, **11**, 846—849).—Berthelot (Abstr., 1901, i, 20) showed that alkali sulphides produce a precipitate of ferrous sulphide in solutions of potassium ferrocyanide. The author finds that this only occurs in the light. Air passed through a solution of potassium ferrocyanide exposed to light precipitates ferric hydroxide. T. E.

Potassium Mercuric Ferrocyanide. Gustave Fernekes (*J. Amer. Chem. Soc.*, 1906, **28**, 87—90).—A detailed account is given of the preparation of *potassium mercuric ferrocyanide*, $K_2HgFe(CN)_6$, by the interaction of mercuric chloride and potassium ferrocyanide. The salt is obtained as a fine, faintly blue powder, is insoluble in water, and is decomposed by hydrochloric acid with formation of Prussian blue, mercuric chloride, and hydroferrocyanic acid; when treated with sodium hydroxide, ferric hydroxide, mercuric oxide, and potassium ferrocyanide are produced. E. G.

Compounds of Hydroferrocyanic, Hydroferricyanic, and Hydrocobalticyanic Acids, with Furfuraldehyde and with Nitrogen Derivatives. Friedrich Wagener and Bernhard Tollens (*Ber.*, 1906, **39**, 410—423. Compare Baeyer and Villiger, Abstr., 1901, i, 658; 1902, i, 112, 355).—Furan and furfuraldehyde yield unstable additive compounds with hydroferrocyanic and hydroferricyanic acids. The composition of the compounds has not been settled, as they readily lose the basic constituent and yield the pure acid.

Trimethylamine cobalticyanide, $2NMe_3,H_3CoC_6N_6,H_2O$, forms a thick, white, crystalline precipitate readily soluble in water, but is thrown down by alcohol; the *ferricyanide* forms small, yellow crystals and begins to decompose at 175°; the *ferrocyanide* crystallises in pale yellow, octahedral crystals and begins to decompose at 140°. Tetramethylammonium hydroxide and hydrocobalticyanic acid yield the *compound* $2NMe_4{\cdot}OH,H_3CoC_6N_6$, which crystallises from hot water in colourless plates. It begins to decompose at 203°. The corresponding *ferricyanide* forms orange-yellow plates and begins to decompose at about 175°. The *ferrocyanide* forms small, pale yellow crystals.

Hexamethylenetetramine cobalticyanide, $2C_6H_{12}N_4,H_3CoC_6N_6,3\frac{1}{2}H_2O$, forms colourless crystals and decomposes at about 160°; *hexamethylenetetramine ferricyanide*, $2C_6H_{12}N_4,H_3FeC_6N_6,2\frac{1}{2}H_2O$, is a reddish-brown precipitate, and the *ferrocyanide*,

$$2C_6H_{12}N_4,H_4FeC_6N_6,7\frac{1}{2}H_2O,$$

is greenish-white.

Pyridine cobalticyanide, $2C_5NH_5,H_3CoC_6N_6,2H_2O$, forms white prisms and decomposes at 175°, the corresponding *ferricyanide* forms yellowish-brown prisms and decomposes at 125°, and the *ferrocyanide* forms yellow prisms decomposing at 135°. *Piperidine cobalticyanide*, $2C_5NH_{11},H_3CoC_6N_6,2H_2O$, crystallises in colourless needles and decomposes at 160°; the *ferricyanide* forms monohydrated, yellow crystals decomposing at 125°, and the *ferrocyanide* (with $1\frac{1}{2}H_2O$), colourless, octahedral crystals decomposing at 125°. *Quinoline cobalticyanide*, $3C_9NH_7,H_3CoC_6N_6,\frac{1}{2}H_2O$, forms colourless crystals decomposing at 190°; the *ferricyanide* (with H_2O), sulphur-yellow crystals, decomposing at 155°, and the *ferrocyanide*, $2C_9NH_7,H_4FeC_6N_6$, yellowish-brown plates.

Betaine cobalticyanide, $2C_5H_{11}O_2N,H_3CoC_6N_6,2H_2O$, forms long, colourless needles, decomposing at 130°; the *ferricyanide* (with $4H_2O$), yellow needles, decomposing at 130°, and the *ferrocyanide* (with $4H_2O$), greenish-white needles decomposing at 140°.

Phenylhydrazine ferrocyanide, $4C_6H_8N_2,H_4FeC_6N_6$, forms colourless, minute plates. J. J. S.

Secondary Arsines. William M. Dehn and Burton B. Wilcox (*Amer. Chem. J.*, 1906, **35**, 1—54).—A method is described for preparing dimethylarsine by the reduction of cacodyl oxide. Dimethylarsine boils at 35·6° under 747 mm. and at 55° under 1·74 atmospheres pressure, and has a sp. gr. 1·213 at 29°.

When dimethylarsine is heated in a sealed tube for an hour at 335° in presence of not more than traces of air, the inner surface of the tube becomes coated with a lustrous, black substance which appears to be the black polymeride of methylarsine described by Auger (Abstr., 1904, i, 724); a gas which is either methane or a mixture of ethane and hydrogen is produced simultaneously.

On allowing dimethylarsine to oxidise slowly in the air, the erytharsine, $(AsCH_3)_4,As_2O_3$, described by Bunsen (*Annalen*, 1842, **42**, 41) is formed. When the arsine is treated with pure oxygen, ethane is produced together with a black solid which consists of a mixture of the polymeride of methylarsine and metallic arsenic. The oxidation is always accompanied by the formation of cacodyl oxide and cacodylic acid.

By the action of bromine on dimethylarsine, hydrogen bromide, hydrogen, and cacodyl bromide are produced together with *bromocacodyl hydrobromide*, $AsMe_2Br,HBr$, which forms white, tabular crystals, is soluble in hot chloroform, insoluble in ether, and is decomposed by water into cacodyl bromide and hydrogen bromide. Chlorine reacts with the arsine with formation of methylarsine dichloride. When dimethylarsine is treated with iodine in a sealed tube, *iodocacodyl hydriodide*, $AsMe_2I,HI$, is obtained, which crystallises in large, pale yellow needles, softens and darkens at 160°, melts at 175°, is soluble in alcohol, and is easily decomposed by water. By the action of aqueous iodine on the arsine, cacodylic acid and hydrogen iodide are produced.

Dimethyldiïsobutylarsonium iodide, $AsMe_2(C_4H_9)_2I$, obtained by heating dimethylarsine with *iso*butyl iodide in a sealed tube at 110° for five hours, is a white, crystalline substance which melts at 155° and is soluble in alcohol or chloroform, but insoluble in ether. *Dimethyldicetylarsonium iodide*, $AsMe_2(C_{16}H_{33})_2I$, forms white crystals and melts at 53—54°. *Dimethyldiïsopropylarsonium iodide*,

$$AsMe_2Pr^{\beta}_2I,$$

is a white, crystalline solid which does not melt below 230°. *Dimethyldiallylarsonium iodide* forms light yellow crystals. *Dimethylallylarsine*, $AsMe_2 \cdot C_3H_5$, obtained by the action of allyl iodide (1 mol.) on dimethylarsine (1 mol.), is a pale yellow liquid which boils at about 160°, is irritating to the eyes and skin, and has a strong, disagreeable odour; when heated with methyl iodide, it is converted into trimethylallylarsonium iodide. Dimethylallylarsine reacts violently with bromine in ethereal solution with formation of the *dibromide*, $C_3H_5 \cdot AsMe_2Br_2$, as a yellow, flocculent precipitate.

The secondary arsines possess basic properties. When dimethylarsine is treated with dry hydrogen bromide at $-10°$, a hydrobromide seems to be formed which readily undergoes decomposition at the ordinary temperature with formation of cacodyl bromide and hydrogen. Dry hydrogen iodide unites with dimethylarsine to form a white, crystalline compound which decomposes into cacodyl iodide and hydrogen. By the action of concentrated sulphuric acid on the arsine, the *sulphate*, $2AsHMe_2,H_2SO_4$, is produced, together with cacodyl sulphide and cacodylic acid.

Nitrous oxide has no action on dimethylarsine, but nitric oxide, nitric peroxide, nitrous acid, and nitric acid react with the base with formation of nitrous oxide or nitrogen, the arsine being converted into various oxidation products, of which cacodylic acid is the most abundant. Chromic acid rapidly oxidises the arsine to dicacodyl or cacodylic acid. An aqueous solution of potassium dichromate is instantly reduced by the arsine. When dimethylarsine is treated with molybdic acid in presence of water, molybdenum dioxide and cacodylic acid are slowly formed. Lead peroxide reacts with the arsine with formation of dicacodyl, lead cacodylate, and lead. Ferric chloride is immediately reduced by the arsine with production of ferrous chloride and cacodyl chloride. If molecular quantities of dimethylarsine and cacodyl chloride are heated together in a sealed tube for two or three hours at 100°, dicacodyl and hydrogen chloride are produced. A study was made of the action of platinic chloride on dimethylarsine, but no definite conclusions could be drawn as to the composition of the products obtained. The compound obtained by Bunsen (*Jahrb. Chem.*, **21**, 500) by the action of platinic chloride on cacodyl chloride, to which he assigned the formula $AsMe_2Cl,PtO,H_2O$, is unstable and varies in composition according to the method of preparation. Auric chloride reacts with dimethylarsine with formation of dicacodyl, cacodyl chloride, cacodylic acid, and a precipitate of indefinite composition. Dimethylarsine rapidly reduces silver nitrate and mercuric chloride to the metal. By the action of potassium ferricyanide on the arsine, potassium ferrocyanide, dicacodyl, and potassium cacodylate are produced. Sulphur reacts readily with the arsine with formation of cacodyl sulphide or disulphide according to the quantity of sulphur used. By the action of liquid sulphur dioxide on the arsine, cacodyl disulphide, methylarsine sulphide, trimethylarsine sulphide, and cacodylic acid are formed. When dimethylarsine is treated with sulphur dichloride, cacodyl chloride, sulphur, and hydrogen sulphide are produced. Stannic chloride reacts with the arsine with formation of hydrogen chloride and the *chlorostannide*, $AsMe_2SnCl_3$, which forms large, colourless needles. By the action of phosphorus trichloride on the arsine, hydrogen chloride, cacodyl chloride, and a compound which is probably $(CH_3P)_x$ or $(CH_3)_2P_4$ are produced. Arsenic trichloride reacts with dimethylarsine with formation of cacodyl chloride, hydrogen chloride, and the compound $(CH_3As)_x$. When the arsine is heated with antimony trichloride, antimony hydride, hydrogen chloride, antimony, and cacodyl chloride are produced. By the action of the arsine on dibromosuccinic acid, cacodyl bromide and succinic acid are formed.

An improved method is described for the preparation of diphenylarsinic acid. Diphenylarsine, obtained by the reduction of diphenylarsinic acid, is a clear, colourless oil which boils at 174° under 25 mm. and at 155° under 37 mm. pressure; it is rapidly oxidised in the air with formation of diphenylarsinic acid and phenylcacodyl oxide. The *tribromide*, $AsPh_2Br_3$, obtained by the action of bromine on the arsine, crystallises in golden-yellow plates, softens at 120°, melts at 129°, and is decomposed by water with formation of phenylcacodyl bromide. *Diphenylarsine iodide*, $AsPh_2I$, was obtained as an oil.

*Basic di*iso*amylarsine chloride*, $6As(C_5H_{11})_2Cl,[As(C_5H_{11})_2]_2O$, obtained by the interaction of *iso*amyl chloride (2 mols.) and arsenic trichloride (1 mol.) in presence of sodium, is a colourless oil which boils at 263° under 750 mm. and at 148° under 33 mm. pressure, has a peculiar odour, and is soluble in the ordinary organic solvents, but insoluble in water; on distilling this compound, a small quantity of a white, soapy, solid substance is formed which is probably iso*amylcacodyl oxide*, $[As(C_5H_{11})_2]_2O$. By the action of bromine on di*iso*amylarsine chloride, the *chlorodibromide*, $As(C_5H_{11})_2ClBr_2$, is obtained, which forms white crystals, is soluble in ether or chloroform, and is slowly dissolved by water with formation of *iso*amylarsinic acid. When di*iso*amylarsine chloride is treated with hydrogen sulphide in presence of water, the *sulphide*, $[As(C_5H_{11})_2]_2S$, is produced, which crystallises in white needles, melts at 29—30°, is easily soluble in ether or carbon disulphide, sparingly so in alcohol, and insoluble in water. iso*Amylarsinic acid*, $(C_5H_{11})_2AsO\cdot OH,2H_2O$, forms large, flaky crystals, melts at 153—154°, and is easily soluble in alcohol, slightly so in water, and insoluble in ether. *Di*iso*amylarsine*, $AsH(C_5H_{11})_2$, obtained by the reduction of di*iso*amylarsinic acid, boils at 150° under 99 mm. pressure, and is oxidised by the air with formation of di*iso*amylarsinic acid and an oil which is probably di*iso*amylcacodyl oxide. E. G.

Preparation of Trialkyl-stibines, -arsines, and -phosphines by the Grignard Reaction. HAROLD HIBBERT (*Ber.*, 1905, **39**, 160—162. Compare Pfeiffer, Abstr., 1905, i, 164; Auger and Billy, *ibid.*, 1904, i, 983).—Good yields (60—70 per cent.) of trimethylstibine may be obtained by the action of magnesium methyl iodide (3 mols.) on an ethereal solution of antimony trichloride cooled in ice and salt. When the product is distilled, the greater part of the stibine passes over with the ether, but the distillation is continued until the temperature of the oil-bath is 170°. Trimethylstibine is immediately thrown down in the form of the crystalline dibromide, $SbMe_3Br_2$, on the addition of bromine.

The ethereal solution of trimethylarsine, when mixed with excess of bromine, yields the perbromide, $AsMe_3Br_4$.

Triethylphosphine may be prepared by using a large excess of magnesium ethyl bromide. When the product is distilled, only 6 per cent. of the phosphine distils over with the ether, the larger portion distils over slowly when the oil-bath is at 160—200°. J. J. S.

[Grignard's Reaction with Dihaloids.] EDMOND E. BLAISE (*Bull. Soc. chim.*, 1906, [iii], **35**, 90—94).—The author claims that some of the observations given as new by Ahrens and Stapler (Abstr., 1905, i, 423, 868) have previously been recorded by himself and others (Abstr., 1901, i, 317; 1905, i, 111. Compare Zelinsky, Abstr., 1903, i, 802, and Archibald and McIntosh, Trans., 1904, **85**, 919). He also questions the probability of some of the conclusions drawn by the authors from these and other results contained in their memoirs on this subject. T. A. H.

Remarkable Difference in the Behaviour of Homologous Cyclic Molecules towards Ammonio-nickel Cyanide. KARL A. HOFMANN and H. ARNOLDI (*Ber.*, 1906, **39**, 339—344. Compare Hofmann and Höchtlen, Abstr., 1903, i, 469).—Whilst benzene, aniline, and phenol interact with ammonio-nickel cyanide, as previously described (*loc. cit.*), the following substances are indifferent to the reagent: toluene, xylene, cumene, ψ-cumene, cymene, mesitylene, hexamethylbenzene, triphenylmethane, naphthalene, anthracene, phenanthrene, fluorene, diphenyl, triphenylmethane, triphenylcarbinol, styrene, amylene, ethylaniline, dimethylaniline, phenylhydrazine, *o*- and *p*-toluidine, anisole, *o*-cresol, nitrobenzene, fluorobenzene, chlorobenzene, bromobenzene, iodobenzene, 2-methylpyridine, and quinoline.

Ammonio-nickel cyanide may be used to test for benzene in petroleum; Russian and American petroleums alone give no precipitate with the reagent, but do so on addition of benzene. When shaken with the reagent, piperidine forms a bluish-white precipitate, $Ni(CN)_2,C_5H_5N$, which evolves pyridine, but not ammonia, when boiled with aqueous potassium hydroxide. Pyrrole forms a colourless, crystalline powder, $Ni(CN)_2,NH_3,C_4H_5N$, which becomes brown on exposure to air and gives the pinewood reaction. Thiophen forms a violet-white, crystalline precipitate, $3Ni(CN)_2,3NH_3,C_4H_4S$. Furan forms a light violet-white, delicate crystalline precipitate, $Ni(CN)_2,NH_3,C_4H_4O$.

A similar difference is shown by benzene and its homologues in their behaviour towards picric acid; this forms additive compounds with benzene and its higher homologues which are solid at or slightly below the ordinary temperature, but not with toluene, *m*-xylene, cumene, ψ-cumene, fluorobenzene, or chlorobenzene.

The benzene-picric acid compound decomposes completely in a few minutes in a vacuum at the ordinary temperature, whereas the benzene ammonio-nickel cyanide remains unchanged during four weeks in a vacuum at the ordinary temperature.

The interaction with ammonio-nickel cyanide appears to depend on the molecular volume of the compound, those which are precipitated having small molecular volumes at 15° : benzene, 88·6 ; aniline, 90·5 ; phenol, 88·8 ; pyridine, 80 ; pyrrole, 69·3 ; thiophen, 78·5 ; and furan, 72 ; whilst those which are not precipitated have large molecular volumes : toluene, 105·6 ; nitrobenzene, 103·6 ; iodobenzene, 110 ; bromobenzene, 105 ; chlorobenzene, 102 ; fluorobenzene, 93·8 ; *o*-toluidine, 107 ; *o*-cresol, 102 ; anisole, 109 ; phenylhydrazine, 97·6 ; α-methylpyridine, 97·6 ; quinoline, 117·8 ; and naphthalene, 111.

G. Y.

Chlorobenzenes as Solvents for Resins. L. E. Andés (*Chem. Rev. Fett. Harz. Ind.*, 1906, **13**, 32—33).—Chlorobenzene readily dissolves galipot (the resin obtained from *Pinus maritima*), colophony, mastic, asphalt, dammar, and metallic resinates. These substances, with the exception of dammar, are also soluble in dichlorobenzene, whilst the following are insoluble in either solvent: shellac, sandarac, copals, benzoin, and amber. The inflammability of both solvents is very slight, they are miscible in all proportions with drying oils, turpentine, &c., and evaporate quickly. A good matt varnish is obtained by dissolving any resin in a mixture of alcohol and chlorobenzene.

W. P. S.

Bromination of Toluene. Arnold F. Holleman and F. H. van der Laan (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, **8**, 512—518).—The authors have investigated quantitatively the influence of temperature, of light, and of bromine carriers on the action of bromine on an excess of toluene. The *o*- and *p*-bromotoluenes and the benzyl bromide formed by the reaction are estimated by the following method. After removal of hydrogen bromide and unchanged bromine by means of a current of air and by treatment with potassium iodide solution and of the excess of toluene by distillation, the benzyl bromide is estimated in a portion of the product by means of alcoholic silver nitrate, with which benzyl bromide interacts to form silver bromide quantitatively. The remainder of the product is shaken with dimethylaniline, washed with dilute nitric acid, dried, and distilled in a vacuum. The solidifying point of the distillate being determined, the amounts of *o*- and *p*-bromotoluene present are found to within 1 per cent. by reference to a solidifying point curve constructed from the results of determinations with mixtures of known composition.

Toluene is brominated in the dark at 25° only slowly, the reaction becoming more rapid as the temperature rises. The product obtained at 25° contains 35·5, 53·9, and 10·6, at 50°, 23·5, 32·8, and 43·7, and at 75°, 6·2, 7·5, and 86·3 per cent. of *o*- and *p*-bromotoluenes and benzyl bromide respectively; the product formed at 100° consists wholly of benzyl bromide.

In diffuse daylight, the bromination proceeds rapidly at 25°, the reaction being completed in about ten minutes. If an excess of toluene is used, the product obtained at 25° contains 99·0, at 100° 99·5, per cent. of benzyl bromide, but if equivalent amounts of toluene and bromine are heated together at the boiling point of toluene, the product contains fractions which boil at higher temperatures.

The experiments with bromine carriers were carried out at 50° and in complete absence of light. The amounts of the carrier added are given in molecular proportion to each mol. of bromine used in the reaction.

With 0·0017, 0·0084, and 0·034 mol. of antimony tribromide, the product contains 22·4, 24·0, and 28·0 per cent. of *o*-bromotoluene, 33·4, 37·8, and 44·1 per cent. of *p*-bromotoluene, and 44·2, 38·2, and 27·9 per cent. of benzyl bromide respectively.

With 0·002, 0·004, 0·006, and 0·017 mol. of aluminium trichloride, the product contains 43·1, 0·5(?), 0, and 0 per cent. of benzyl bromide, the mixture of bromotoluenes consisting of 43·9, 44·6, 44·3, and 49·2 per cent. of the ortho- and 56·1, 55·4, 55·7, and 50·1 per cent. of the para-isomeride respectively.

With 0·0007, 0·001, and 0·002 mol. of ferric bromide, the product contains 40·8, 7·8, and 0 per cent. of benzyl bromide, whilst with 0·0007, 0·002, 0·006, and 0·01 mol. of this carrier the mixture of bromotoluenes contains 36·9, 36·0, 37·9, and 37·0 per cent. of the ortho- and 63·1, 64·0, 62·1, and 63·0 per cent. of the para-isomeride respectively.

On the other hand, with 0·02 mol. of phosphorus tribromide, the product contains 54·7 per cent. benzyl bromide, the mixture of bromotoluenes consisting of 41·4 and 58·6 per cent. of the ortho- and para-isomerides respectively. G. Y.

Ortho-substituted Iodo-compounds with Uni- and Multivalent Iodine. CONRAD WILLGERODT and MAX SIMONIS (*Ber.*, 1906, **39**, 269—280).—m-*Nitro*-p-*tolyl iododichloride*, $NO_2\cdot C_6H_3Me\cdot ICl_2$, prepared by passing dry chlorine into a well-cooled chloroform solution of *p*-iodo-*m*-nitrotoluene, crystallises in large, yellow, lustrous plates and decomposes at 71°; by aqueous sodium hydroxide, it is converted into p-*iodoso*-m-*nitrotoluene*, $NO_2\cdot C_6H_3Me\cdot IO$, which is a stable, intensely red powder exploding at 129°; the *acetate*, $NO_2\cdot C_6H_3Me\cdot I(OAc)_2$, forms bright yellow, slender needles, and, when dry, explodes at 200°; the *basic sulphate*, $C_{14}H_{14}O_{10}N_2I_2S$, forms crystalline crusts and decomposes at 91°; the *basic nitrate*, $C_7H_7O_6N_2I$, melts and decomposes at 132°; the *basic iodide*, $C_7H_7O_6NI_2$, begins to decompose at 80°; the basic *chromate* explodes at 94° and the *formate*, $C_9H_8O_6NI$, at 72°.

p-*Iodoxy*-m-*nitrotoluene*, $NO_2\cdot C_6H_3Me\cdot IO_2$, prepared by decomposing the iodochloride with a solution of sodium hydroxide and sodium hypochlorite, crystallises from water or glacial acetic acid in long, slender, colourless needles and detonates at 196·5°.

Di-m-*nitro*-p-*tolyliodinium hydroxide* is obtained in solution by the action of moist silver oxide on a mixture of *p*-iodoxy- and *p*-iodoso-*m*-nitrotoluene; the *iodide*, $I(C_6H_3Me\cdot NO_2)_2I$, crystallises from water in slender, colourless needles and decomposes at 51°.

Phenyl m-*nitro*-p-*tolyliodinium hydroxide* is prepared from iodoxybenzene and *p*-iodoso-*m*-nitrotoluene in a similar manner.

p-*Iodo*-m-*toluidine*, prepared by heating *p*-iodo-*m*-nitrotoluene with freshly precipitated ferrous hydroxide and alcohol, crystallises from dilute alcohol, melts at 48°, and is nearly colourless. The *hydrochloride* forms pale yellow needles, the *nitrate* red needles, the sulphate is colourless; the *oxalate*, $2C_7H_8NI,H_2C_2O_4$, melts at 113°. p-*Iodo*-m-*acetotoluidide* crystallises from acetic acid in slender, colourless needles and melts at 145—146°; p-*iodo*-m-*formotoluidide* is similar and melts at 129°.

On chlorinating *p*-iodo-*m*-toluidine in chloroform solution, a definite product cannot be isolated, but on similarly chlorinating *p*-iodo-*m*-acetotoluidide, 6-*chloro*-4-*iodo*-m-*acetotoluidide* is obtained; it crystallises from benzene or glacial acetic acid in fan-like aggregates of small, colourless needles, melts at 196·5°, and combines with chlorine to form the *iododichloride*, $NHAc\cdot C_6H_2MeCl\cdot ICl_2$, which on warming loses chlorine and regenerates 6-chloro-4-iodo-*m*-acetotoluidide. On hydrolysis, the acetyl derivative gives 6-*chloro*-4-*iodo*-m-*toluidine*, which crystallises from dilute alcohol in thin, colourless plates, melts at 65°, and gives an *oxalate*, $C_{16}H_{16}O_4Cl_2N_2I_2$, crystallising in large plates and melting at 165°. On replacing the amino-group by chlorine, oxidising the 3:6-dichloro-4-iodotoluene so formed, and decomposing the dichloroiodobenzoic acid, 1:4-dichloro-2-iodobenzene, melting at 20°, is obtained.

3:4-*Di-iodotoluene*, prepared from 4-iodo-*m*-toluidine through the diazo-reaction, crystallises from alcohol in flat, colourless needles and melts at 117·5°. On chlorination, only the *monoiododichloride*,

$$C_6H_3MeI\cdot ICl_2,$$

is obtained, a di-iododichloride not being formed; attempts to convert this chloride into the corresponding iodoso- and iodoxy-compounds were without successful issue. W. A. D.

Certain Derivatives of Benzenesulphonylaminoacetonitrile. Treat B. Johnson and Elmer V. McCollum (*Amer. Chem. J.*, 1906, 35, 54—67).—Benzenesulphonylaminoacetonitrile (Knoevenagel and Lebach, Abstr., 1904, i, 994) may be prepared by treating aminoacetonitrile with benzenesulphonic chloride; it melts at 80°.

By the action of methyl iodide on the silver derivative of this compound, *benzenesulphonylmethylaminoacetonitrile*, $SO_2Ph\cdot NMe\cdot CH_2\cdot CN$, is obtained, which crystallises from water in plates, melts at 97°, and is readily hydrolysed by hydrochloric acid. *Benzenesulphonylmethylaminoacetic acid*, $SO_2Ph\cdot NMe\cdot CH_2\cdot CO_2H$, crystallises from hot water in prisms and melts at 179°; its *ethyl* ester boils at 215—216° under 15 mm. pressure. When this acid is boiled with hydrochloric acid for fifteen hours, sarcosine benzenesulphonate is obtained.

Benzenesulphonylethylaminoacetonitrile, $SO_2Ph\cdot NEt\cdot CH_2\cdot CN$, boils and suffers partial decomposition at 225—235° under 21 mm. pressure;

the corresponding *acid* crystallises from water in colourless plates and melts at 116°.

*Benzenesulphonyl-*n*-propylaminoacetonitrile* was obtained as an oil which, on hydrolysis, yielded the corresponding *acid*, which crystallises in stout prisms and melts at 99—101°.

Benzenesulphonylcarbethoxyaminoacetonitrile,

$$SO_2Ph\cdot N(CO_2Et)\cdot CH_2\cdot CN,$$

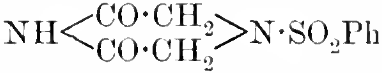
obtained by the action of ethyl chloroformate on the potassium derivative of benzenesulphonylaminoacetonitrile, crystallises from alcohol in needles, melts at 83—85°, and when heated with solution of sodium hydroxide and afterwards acidified with hydrochloric or sulphuric acid, is reconverted into benzenesulphonylaminoacetonitrile.

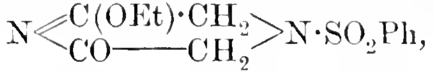
Benzenesulphonylbenzylaminoacetonitrile forms colourless prisms and melts at 68—70°; the corresponding *acid* crystallises in needles and melts at 123—125°.

*Benzenesulphonyl-*p*-nitrobenzylaminoacetonitrile* crystallises in prisms and melts at 123—125°; the *acid* forms hair-like needles and melts and decomposes at 210—212°.

Ethyl benzenesulphonylcyanomethylaminoacetate,

$$SO_2Ph\cdot N(CH_2\cdot CN)\cdot CH_2\cdot CO_2Et,$$

obtained by the action of ethyl chloroacetate on benzenesulphonylaminoacetonitrile, crystallises in radiating needles and melts at 68—70°. When this ester is warmed with solution of sodium hydroxide until it has completely dissolved and is subsequently acidified with hydrochloric or sulphuric acid, 2 : 6-*diketo*-4-*benzenesulphonylpiperazine*,  $NH{<}{\begin{smallmatrix}CO\cdot CH_2\\ CO\cdot CH_2\end{smallmatrix}}{>}N\cdot SO_2Ph$, is produced, which crystallises in prisms, melts and decomposes at 198—199°, and when heated with strong hydrochloric acid in a sealed tube for two hours at 140—150° is converted into iminodiacetic acid, which melts and decomposes at 235—236°. 2-*Ethoxy*-4-*benzenesulphonyl*-6-*ketopiperazine*,



$$N{\ll}{\begin{smallmatrix}C(OEt)\cdot CH_2\\ CO\text{——}CH_2\end{smallmatrix}}{>}N\cdot SO_2Ph,$$

obtained by the action of ethyl iodide on the silver derivative of 2 : 6-diketo-4-benzenesulphonylpiperazine, crystallises in pyramids and melts at 130—132°.

Benzenesulphonylbenzoylaminoacetonitrile, $SO_2Ph\cdot NBz\cdot CH_2\cdot CN$, forms radiating needles, melts at 110—112°, and when boiled with concentrated hydrochloric acid is converted into a mixture of benzoic and benzenesulphonylaminoacetic acids. Phosphorus pentachloride reacts with benzenesulphonylaminoacetic acid with formation of benzenesulphonylaniline.

Carbethoxyaminoacetonitrile, $CO_2Et\cdot NH\cdot CH_2\cdot CN$, obtained by the action of ethyl chloroformate on the sulphate of aminoacetonitrile in presence of sodium hydroxide, boils at 175° under 35 mm. pressure, crystallises in radiating prisms, and melts at 48—50°.

An attempt was made to effect the condensation of benzenesulphonylaminoacetic acid with catechol, but without success. E. G.

Molecular Compounds of Nitro-compounds with Amines.

EMILIO NOELTING and E. O. SOMMERHOFF (*Ber.*, 1906, **39**, 76—79. Compare Hepp, Abstr., 1883, 315; van Romburgh, Abstr., 1895, i, 652; Sudborough, Trans., 1901, **79**, 522; Sachs and Steinert, Abstr., 1904, i, 506).—The authors have prepared a number of *additive compounds* from 1 mol. of trinitrobenzene with 1 mol. of each of the amines mentioned below. The colours and crystalline forms are those of the additive compounds; the temperatures given are the melting points.

o-Toluidine: light red needles, 125—127°; *m*-toluidine: light red needles, 93°; *p*-toluidine: dark red needles, easily decomposed; *o*-3-xylidine: red needles, 125—128°; *m*-4-xylidine: brownish-red needles, 96—98°; *m*-2-xylidine: light red needles, 118—120°; *p*-xylidine: red needles, 100—101°; mesidine: brownish-red needles, 120—122°; ψ-mesidine: dark brownish-red needles, 108—110°; 5-*tert*.-butyl-*m*-2-xylidine: brown needles, 120—122°; benzidine: black needles; tolidine: black needles, 178°; dimethyl-*p*-toluidine: black needles, 124°; *o*-phenylenediamine: brown needles, 175°; *m*-phenylenediamine: brown needles; *p*-phenylenediamine: blackish-brown needles; *m*-tolylenediamine: brown needles; *m*-xylylene-4:6-diamine: blackish-brown needles; 4-amino-1-toluquinoline: black needles; tetrahydroquinoline: dark red needles.

Aromatic diamines do not form additive compounds with 2 mols. of trinitrobenzene. Additive compounds are not formed by trinitrobenzene with *p*-bromoaniline, bromo-*m*-xylidine, azobenzene, or the nitro-*o*-toluidines. The following amines form *additive* compounds with 2 mols. of trinitrobenzene:

Diphenylamine: glistening, black plates, 109—110°; *p*-ditolylamine: glistening, black plates; quinoline: white needles, readily decomposed; 1:2-xyloquinoline: long, white needles, 113°.

The *additive* compounds of 1 mol. of trinitrotoluene with 1 mol. of the following amines are formed less readily and are less stable than the additive compounds of trinitrobenzene:

o-Toluidine: light red needles, 53—55°; *m*-toluidine: light red needles, 62—63°; *m*-4-xylidine: red needles, 43—45°; ψ-cumidine: stable, brown needles; dimethyl-*p*-toluidine: bluish-black needles.

When mixed in molecular proportions in alcoholic solution at the laboratory temperature, trinitrobenzoic acid and ψ-cumidine form a colourless *salt*, which, when warmed, loses carbon dioxide and yields the red additive compound of trinitrobenzene and ψ-cumidine. But when heated together in methyl-alcoholic solution on the water-bath, trinitrobenzoic acid and ψ-cumidine form a brown *additive compound*, which melts at 140—143° and dissolves in warm hydrochloric acid to form a red solution. The basic component of this compound can be titrated with sodium nitrite solution.

With freshly distilled, colourless aniline, nitrobenzene, *p*-nitrotoluene, and *m*-dinitrobenzene give intense red colorations which disappear on adding alcohol. G. Y.

Formation of Anilides. Heinrich Goldschmidt and Robert Bräuer (*Ber.*, 1906, **39**, 97—108. Compare Goldschmidt and Wachs, Abstr., 1898, ii, 67).—Experiments with aniline or *o*-toluidine and *n*-butyric or *iso*butyric acid at 100° show that the formation of the anilide is a reaction of the second order, whereas on addition of picric acid it becomes unimolecular. The rate of formation of the anilides and *o*-toluidides, with or without the addition of picric acid, diminishes for the four acids investigated, in the order: acetic, propionic, *n*-butyric, and *iso*butyric acid.

As the reaction between formic acid and aniline at 100° is completed in a few minutes, the experiments with this acid and aniline or *o*-toluidine were carried out at 45—55°. As with the above-mentioned aliphatic acids, the reaction is bimolecular, but on addition of picric acid an increase in the velocity of the reaction is observed only if the concentration of the catalyst is not less than that of the formic acid. It may be that in the formation of anilides in presence of a catalytic agent the two reactions of the first and second orders, respectively, take place together, in which case the velocity of the whole reaction is represented by the equation: $\frac{dx}{dt} = k(a-x)c + k'(a-x)^2$, in which k and k' are products of the velocity constants with the constants of equilibrium which determine the different states in which the aliphatic acid exists in the basic solvent.

The reaction between formic acid and aniline in presence of picric acid does not stop at the formation of the anilide, but proceeds to that of diphenylformamidine. G. Y.

Kinetics of the Fission of Carbon Dioxide from Trichloroacetic Acid in Aniline Solution. HEINRICH GOLDSCHMIDT and ROBERT BRÄUER (*Ber.*, 1906, **39**, 109—112. Compare preceding abstract; Silberstein, Abstr., 1885, 160; Balcom, *Inaug. Diss.*, Heidelberg, 1905).—Contrary to the behaviour of acetic acid and its homologues with aniline, the interaction of trichloroacetic acid and aniline at 25—45° is unimolecular, and leads to the formation of carbon dioxide and chloroform. The velocity of the reaction is influenced to only a slight extent by the addition of strong acids; thus the value of k for the reaction in presence of picric acid at 25° is slightly greater than the value obtained without addition of picric acid, whilst at 45° the two values of k are identical. G. Y.

Action of Hydrogen Peroxide on Sulphuric Acid Solutions of Diphenylamine. A. USCHAKOFF (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 913—915).—The action of a solution of hydrogen peroxide on a concentrated sulphuric acid solution of diphenylamine yields: (1) the *compound* $C_{24}H_{20}O_2N_2$, which is soluble in 5 per cent. potassium hydroxide solution and also in concentrated sulphuric acid, to which it imparts a blue colour; on reduction with zinc dust and acetic acid or with sodium and alcohol, diphenylamine is not formed, but the violet colour of the solution changes to pale yellow, which, in presence of air or water, again becomes violet; (2) the *compound* $C_{60}H_{49}O_2N_5$, which is an amorphous, violet powder, melting at above 100°; with sulphuric acid, it behaves like compound (1), and when heated with zinc dust it yields a small proportion of diphenylamine, certain oily products, and from 10 to 20 per cent. of a *compound* crystallising from ethyl acetate in silvery, hexagonal plates which melt at 240°. T. H. P.

Diphenylamine Nitrates. A. Uschakoff (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 911—912).—The *salt* $3NHPh_2,2HNO_3$ forms well-developed crystals melting at 102—103° and dissolves in alcohol, ether, aniline, or acetic acid; it is decomposed by boiling water and turns blue in the air. The *salt* $4NHPh_2,HNO_3$ has the melting point 54°, the same as diphenylamine itself, indicating that it decomposes before melting. T. H. P.

Terpenes and Ethereal Oils. LXXV. Conversion of Ketones and Aldehydes into Bases. Otto Wallach [with Karl Hüttner and Johannes Altenburg] (*Annalen*, 1905, **343**, 54—74).—The conversion of ketones and aldehydes into bases by treatment with ammonium formate is represented as follows: $COR_2 + NH_3 = OH{\cdot}CR_2{\cdot}NH_2$; $OH{\cdot}CR_2{\cdot}NH_2 + HCO_2H = CHR_2{\cdot}NH_2 + CO_2 + H_2O$, the free formic acid acting as a reducing agent. This view of the reaction accounts for the fact that secondary and tertiary bases are formed with the primary base; the primary base reacts with the aldehyde or ketone in the place of the ammonia. Since the reaction depends on the base being free and uncombined with acids, the presence of acids affects the course of the reaction. Generally under the conditions at which these reactions occur, the salts of the primary bases are less dissociated than ammonium salts, and hence the reaction between ammonia and the aldehyde or ketone predominates, but small amounts of secondary (or tertiary) bases are then produced.

It has been found (i) that the addition of anhydrous formic or acetic acid to the mixture of the ammonium formate and aldehyde or ketone leads to a single product, the primary amine; (ii) that the reaction will take place at a low temperature, and accordingly the formation of formyl derivatives is avoided; aromatic bases form such derivatives at any temperature at which the reaction will take place. (iii) The reaction can be used with all ketones and aldehydes and all classes of bases, and can thus be used in the preparation of mixed secondary and tertiary bases.

Diethylmethylamine [γ-aminopentane], $CHEt_2{\cdot}NH_2$, was prepared from diethyl ketone and ammonium formate, the two substances being boiled together in the presence of a little acetic acid. *Formyl-α-phenylethylamide*, $CHMePh{\cdot}N{\cdot}OCH$, was prepared from acetophenone and ammonium formate at 155°, and is an oil boiling at 200° under 14 mm. pressure; in the presence of acetic acid, α-phenylethylamine is obtained. *cyclo*Hexanone and ammonium formate in the presence of acetic acid yield mainly di*cyclo*hexylamine, $NH(C_6H_{11})_2$, which is a liquid boiling at 251—252°, and has a sp. gr. 0·925 and n_D 1·4861 at 18°; the nitrate, oxalate, and thiocyanate are sparingly soluble; the *nitrosoamine*, $N(C_6H_{11})_2{\cdot}NO$, is characteristic and melts at 105—106°. *Benzyl*cyclo*hexylamine*, $C_6H_{11}{\cdot}NH{\cdot}CH_2Ph$, prepared by boiling for four hours *cyclo*hexanone, benzylamine, and formic acid, is a colourless liquid boiling at 281—282°; its *formyl* derivative is produced at the same time.

1-Methyl*cyclo*hexane-3-one and ammonium formate in the presence of acetic or formic acid yield the secondary base, *di-1-methyl*cyclo*hexyl-3-amine*, $NH(C_6H_{10}Me)_2$, which boils at 134—135° under 12—14 mm.

and at 273° in an atmosphere of hydrogen under the ordinary pressure; it has a sp. gr. 0·8878 and n_D 1·4756 at 21°; the base appears to be a mixture of stereoisomeric compounds. The same mixture can be obtained by heating together the methyl*cyclo*hexanone and methylhexylamine formate and formic acid.

Amylamine and the methyl*cyclo*hexanone in the presence of formic acid give 1-*methyl*cyclo*hexylamylamine*, $C_5H_{11}·NH·C_6H_{10}Me$, which boils at 234°. 1-Methyl*cyclo*hexanone-3 and benzylamine yield *benzyl*-1-*methyl*cyclo*hexyl-3-amine*, $C_6H_{10}Me·NH·CH_2Ph$, which boils at 165—170° under 12 mm. pressure and has a sp. gr. 0·946 and n_D 1·5182 at 22°.

Tri*iso*amylamine is formed from valeraldehyde, ammonium formate, and formic acid, and tribenzylamine from benzaldehyde and ammonium formate and formic acid. Valeraldehyde and aniline formate give formanilide and *diamylaniline*, $NPh(C_5H_{11})_2$, which boils at 264—265°. Methylamylaniline is obtained from valeraldehyde and methylaniline formate.

At low temperatures, benzaldehyde and aniline formate yield benzylaniline, $CH_2Ph·NHPh$, which melts at 32° and yields a *nitrosoamine* melting at 57°. *Formylbenzylanilide*, which is mainly produced at higher temperatures, melts at 48°.

Methyl*cyclo*hexylamine formate and benzaldehyde in the presence of formic acid yield, at 160°, the same benzylmethyl*cyclo*hexylamine which is formed in the interaction of methylhexanone and *cyclo*hexylamine. Benzaldehyde and ethylamine formate give benzylethylamine, and with piperidine formate, benzylpiperidine boiling at 248°.

K. J. P. O.

Asymmetric Nitrogen. XXII. Optically Active Ammonium Salts. Edgar Wedekind (*Ber.*, 1906, **39**, 474—480. Compare this vol., i, 14).—*l*-Phenylbenzylmethylpropylammonium iodide and *l*-phenylbenzylmethyl*iso*butylammonium iodide respectively were examined crystallographically, and no hemihedrism was detected in either case. *l*-Phenylbenzylmethylpropylammonium bromide, prepared by the addition of potassium bromide to a solution of *l*-phenylbenzylmethylpropylammonium *d*-bromocamphorsulphonate, when crystallised either from water or from alcohol also shows no tendency to hemihedrism; the specimen which was crystallised from water was isomorphous with the iodide described, whilst the specimen crystallised from alcohol had a different crystalline form.

The tendency to autoracemisation exhibited by various optically active ammonium salts investigated by the author in chloroform solution is characteristic with the chlorides, bromides, and iodides; the nitrates, however, are optically stable. d-*Phenylbenzylmethylpropylammonium nitrate*, prepared by the addition of silver nitrate to an alcoholic solution of the *d*-iodide, forms colourless crystals and decomposes at 170°; it has $[\alpha]_D$ +114° in chloroform solution, a value which exhibited practically no variation when the solution remained at the laboratory temperature for two days. Solutions of the corresponding chloride, bromide, and iodide respectively all exhibited autoracemisation, the phenomenon being more marked with the iodide than with the bromide. The fluoride does not appear to undergo any marked autoracemisation. The free base, *l*-phenylbenzylmethyl*iso*butylammonium hydroxide, undergoes autoracemisation in chloroform solution more slowly than does its iodide. A. McK.

Asymmetric Nitrogen. XXIII. Isomerism with Asymmetric Ammonium Salts. EDGAR WEDEKIND (*Ber.*, 1906, **39**, 481—488. Compare preceding abstract).—Whilst *o*-methoxyphenylbenzylmethylallylammonium iodide may be prepared from benzyl iodide and methylallyl-*o*-anisidine or from allyl iodide and benzylmethyl-*o*-anisidine, the product obtained from methyl iodide and benzylallyl-*o*-anisidine consists of anisyltrimethylammonium iodide. This observation, taken in conjunction with the results obtained by Jones (Trans., 1905, **87**, 1721), led the author to re-examine the case of isomerism which he thought he had discovered with phenylbenzylmethylallylammonium iodide; the so-called "*β*-iodide" is now shown to be phenylbenzyldimethylammonium iodide, which decomposes at 164—165°. The analyses, formerly made by the author with the "*β*-iodide," were made with a mixture of phenylbenzyldimethylammonium iodide and the normal phenylbenzylmethylallylammonium iodide. Optically inactive isomerides of phenylbenzylmethylallylammonium iodide accordingly do not exist.

[With EMANUEL FRÖHLICH.]—*Methylallyl-*o*-anisidine*, prepared from allyl iodide and methyl-*o*-anisidine, is a yellow oil which boils at 167° under 85 mm. pressure; its *picrate* melts at 139°.

*Benzylmethyl-*o*-anisidine*, prepared from benzyl bromide and methyl-*o*-anisidine, is a viscid, yellow oil which boils at 217—220° under 65 mm. pressure; its *picrate* melts at 129°.

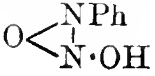
*Benzyl-*o*-anisidine*, prepared from benzyl chloride and *o*-anisidine or from benzyl chloride, *o*-anisidine, and potassium hydroxide, is a viscid, yellow oil which boils at 217—220° under 25 mm. pressure; its picrate melts at 137°.

*Benzylallyl-*o*-anisidine*, prepared from allyl iodide, benzyl-*o*-anisidine, and potassium hydroxide, boils at 205—206° under 50 mm. pressure.

o-*Methoxyphenylbenzylmethylallylammonium iodide*, prepared from benzyl iodide and methylallyl-*o*-anisidine, is identical with the compound obtained from allyl iodide and benzylmethyl-*o*-anisidine and decomposes at 120°.

Anisyltrimethylammonium iodide, obtained from methyl iodide and benzylallyl-*o*-anisidine, decomposes and sublimes at about 210—220°.

A. McK.

Certain Nitrogen Compounds. ANGELO ANGELI and VINCENZO CASTELLANA (*Atti R. Accad. Lincei*, 1905, [v], **14**, ii, 657—660).—Angeli and his collaborators have shown (Abstr., 1905, i, 873) that, in the form of salts, nitrosophenylhydroxylamine, $NO\cdot NPh\cdot OH$, and phenylnitroamine (phenylnitroamic acid), $NHPh\cdot NO_2$, have the structures $O\colon NPh\colon N\cdot OH$ and $NPh\colon NO\cdot OH$ respectively. These differ as regards the position which the oxygen atom takes up in the diazobenzene hydroxide, $NPh\colon N\cdot OH$, from which they are derived. Since some authorities ascribe the structure  $O<\begin{matrix}NPh\\ |\\ N\cdot OH\end{matrix}$ to phenylnitroamic acid, it is seen that this substance stands in very close relationship to the aromatic azoxy-compounds, which contain the ring

united to two radicles, generally identical. Asymmetric or mixed azoxy-compounds, $R(N_2O)R'$, which are very difficult to prepare, should exist in only one modification if they contain the N_2O ring, whilst if their constitution is analogous with that of nitrosophenylhydroxylamine two isomerides should be possible.

By condensing nitrobenzene and aniline, the authors have obtained, besides azoxybenzene, a brownish-red oil which does not reduce Fehling's solution, is decomposed by hydrochloric acid into nitrobenzene and aniline, and is probably a condensation product of the formula $O:NPh(OH)\cdot NHPh$. Nitrobenzene reacts in a similar way with *p*-toluidine.

To the condensation products of aldehydes with substituted hydroxylamines, Bamberger attributes a structure,

$O<\begin{matrix}CHR\\|\\NR\end{matrix}$, analogous with that of the azoxy-compounds. The authors find that the product obtained from benzaldehyde and phenylhydroxylamine forms an additive *compound*, melting at 170°, with 1 mol. of phenylcarbimide, a fact which is best explained if the compound has the structure

$$CHPh:N\cdot C_6H_4\cdot OH,$$

since this does not require intramolecular change to be effected by the phenylcarbimide. Confirmation of this conclusion is obtained in the behaviour of phenylhydroxylamine, which combines with 1 mol. of phenylcarbimide to give a *compound*, melting at 126°, soluble in alkali, and capable of reducing Fehling's solution, the reduction being accompanied by the odour of nitrosobenzene. Phenylcarbimide does not, therefore, determine the transposition of phenylhydroxylamine into *p*-aminophenol, since, if this were effected, two molecules of the carbimide should participate in the reaction and no odour of nitroso-compound should be observed. T. H. P.

Action of Carbamide on Compounds of Cyanoacetic Acid.

GUSTAV FRERICHS and L. HARTWIG (*J. pr. Chem.*, 1906, [ii], 73, 21—48. Compare this vol., i, 74).—When heated with aniline over a naked flame, the ethyl ester, $C_6H_8O_3N_2$, melting at 162° (*loc. cit.*), yields *s*-diphenylcarbamide, a small quantity of *s*-diphenylbiuret, and a dibasic *acid*, $C_{30}H_{24}O_3N_6$, which forms white leaflets, melts at 195°, and gives an intense red coloration with alcoholic ferric chloride. The action of aniline on the methyl ester, $C_5H_6O_3N_2$, melting at 128° (*loc. cit.*), leads to the formation of the same products. The *sodium*, *potassium*, and *silver* salts of the dibasic acid were analysed; its *diethyl* ester, $C_{30}H_{22}O_3N_6Et_2$, formed by the action of ethyl iodide and alcoholic potassium hydroxide on the acid, crystallises in white needles and melts at 158°; the *dibenzyl* ester, $C_{30}H_{22}O_3N_6(CH_2Ph)_2$, crystallises in white needles and melts and decomposes at 215°. When hydrolysed with concentrated hydrochloric acid or with 10 per cent. aqueous potassium hydroxide, the dibasic acid yields ammonia and aniline; no other organic substance could be detected amongst the products of the hydrolysis.

When heated with *p*-toluidine, the ethyl ester, $C_6H_8O_3N_2$, forms *p*-tolylcarbamide, *s*-di-*p*-tolylcarbamide, and a dibasic *acid*, $C_{33}H_{30}O_3N_6$, which crystallises in white leaflets, melts at 221°, and gives a red coloration with alcoholic ferric chloride.

With *m*-toluidine, the ethyl ester, $C_6H_8O_3N_2$, yields *m*-tolylcarbamide, *s*-di-*m*-tolylcarbamide, and a dibasic *acid*, $C_{33}H_{30}O_3N_6$, which crystallises in glistening, colourless leaflets, melts at 186°, and gives a red coloration with alcoholic ferric chloride.

The dibasic *acid*, $C_{30}H_{21}O_3N_6Cl_3$, formed by heating the ethyl ester, $C_6H_8O_3N_2$, with *m*-chloroaniline, is obtained as a crystalline powder melting at 217°. When treated with benzyl chloride and alcoholic potassium hydroxide, it yields the *dibenzyl* ester, $C_{20}H_{19}O_3N_6Cl_3(CH_2Ph)_2$, which crystallises in needles, melts at 186—188°, and is insoluble in aqueous ammonia or dilute alkali hydroxides.

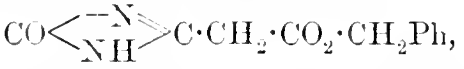
When heated with *m*-bromoaniline, the ethyl ester, $C_6H_8O_3N_2$, yields a mixture of *m*-bromophenylcarbamide and *s*-di-*m*-bromophenylcarbamide and the dibasic *acid*, $C_{30}H_{21}O_3N_6Br_3$, which is obtained on acidification of its ammoniacal solution as a white, crystalline powder, and when heated with benzyl chloride and alcoholic potassium hydroxide on the water-bath forms the *dibenzyl* ester, $C_{30}H_{19}O_3N_6Br_3(CH_2Ph)_2$; this crystallises in white needles and melts at 185—187°.

When heated with an excess of methylaniline, the ethyl ester,

$$C_6H_8O_3N_2,$$

yields (1) its ammonium salt; this must be due to partial decomposition of the acid, yielding cyanic acid, which interacts with methylaniline to form *s*-diphenyldimethylcarbamide and ammonia; and (2) a dibasic *acid*, $C_{23}H_{30}O_3N_6$, which forms thick, yellow, rhombic crystals, melts at 175°, and gives a red coloration with alcoholic ferric chloride. The same products are obtained by the action of methylaniline on the methyl ester, $C_5H_6O_3N_2$.

The ethyl ester, $C_6H_8O_3N_2$, interacts with an excess of warm benzyl alcohol to form: (1) the *benzyl* ester,



$$CO{<}{\overset{-N=}{\underset{NH}{}}}{>}C\cdot CH_2\cdot CO_2\cdot CH_2Ph,$$

which crystallises from dilute alcohol in colourless octahedra or broad, flat, denticulate aggregates and melts and decomposes at 148°, and (2) a *substance*, $C_{17}H_{13}O_5N$, which crystallises in flat, white needles, melts at 267°, and with ferric chloride in aqueous solution forms a reddish-violet precipitate which dissolves in alcohol, forming a dark red solution which gradually deposits dark violet prisms.

When heated at 180°, the ethyl ester, $C_6H_8O_3N_2$, melts and evolves at first alkaline, but later acid, vapours having an odour of ethyl cyanoacetate; the distillate gives the iodoform reaction. The *residue* consists of a white, crystalline powder, $C_8H_7O_4N_3$ (?), which decomposes at high temperatures, becoming yellow and finally black; it is soluble in aqueous ammonia, from its solution in which it is reprecipitated by addition of hydrochloric acid; it does not give the murexide reaction and does not give the reaction products of cyanic acid when heated with aniline, but yields bromoform and ammonium bromide when treated with bromine water.

When heated with carbamide, cyanoacetic acid forms cyanoacetylcarbamide, or, on prolonged heating, uric acid (compare Formánek, Abstr., 1892, 149). A number of experiments intended to throw light on the mechanism of this reaction yielded only negative results. G. Y.

Hexahydrothiophenol (*cyclo*Hexyl Mercaptan). Walther Borsche and W. Lange (*Ber.*, 1906, **39**, 392—397. Compare Abstr., 1905, i, 766).—The yield of *cyclo*hexyl hydrosulphide obtained by reducing *cyclo*hexanesulphonic chloride with tin and hydrochloric acid is some 40—50 per cent. of the theoretical. Only a small amount of the mercaptan is formed when *cyclo*hexyl bromide is heated with an alcoholic solution of potassium hydrogen sulphide, the chief product being *cyclo*hexene

cyclo*Hexyl xanthate*, $C_6H_{11}S\cdot CS\cdot OEt$, is obtained as a yellow oil distilling at 150—153° under 16 mm. pressure when *cyclo*hexyl bromide is warmed with an alcoholic solution of potassium xanthate. A small amount of cyclo*hexyl trithiocarbonate*, $CS(S\cdot C_6H_{11})_2$, is also formed. It crystallises from alcohol in yellow needles and melts at 75—76°.

Ammonia converts *cyclo*hexyl xanthate into *cyclo*hexyl mercaptan and xanthamide,

$$C_6H_{11}S\cdot CS\cdot OEt + NH_3 = NH_2\cdot CS\cdot OEt + C_6H_{11}\cdot SH.$$

The mercaptan is a colourless oil distilling at 158—160° and is lighter than water. The *mercuric* compound, $C_6H_{11}S\cdot HgCl$, is obtained as a white precipitate on the addition of an alcoholic solution of mercuric chloride to the mercaptan dissolved in alcohol. cyclo*Hexyl methyl sulphide*, $C_6H_{11}\cdot SMe$, is a colourless oil distilling at 179—180°. cyclo*Hexyldimethylsulphonium iodide*, $C_6H_{11}SMe_2I$, forms small crystals melting at 102°. It is deliquescent and dissolves readily in methyl or ethyl alcohol, but only sparingly in ether. The corresponding *hydroxide*, $C_6H_{11}\cdot SMe_2\cdot OH$, melts at about 80°, the *chloride* at about 90°, and the *platinichloride*, $(C_6H_{11}SMe_2)_2,PtCl_6$, at 136°. The last compound crystallises from water in brick-red needles. J. J. S.

[4-Nitro-2-amino-6-acetylaminophenol.] Leopold Cassella & Co. (D.R.-P. 161341).—Acetic anhydride reacts with sodium picramate at 60° to form sodium acetylpicramate, which is reduced by sodium sulphide at 80°, and acids then precipitate 4-*nitro*-2-*amino*-6-*acetylaminophenol*, sparingly soluble in alcohol, more readily in ether or acetic acid. Acids hydrolyse it to 4-nitro-2 : 6-diaminophenol. The diazonium compound forms sparingly soluble yellow crystals and may be used for the preparation of azo-dyes. C. H. D.

Nitration of Benzoyl- and Dibenzoyl-*p*-aminophenol. Frédéric Reverdin and Ernest Delétra (*Ber.*, 1906, **39**, 125—129. Compare Reverdin and Dresel, Abstr., 1905, i, 51, 430).—2 : 6-*Dinitro*-4-*benzoylaminophenol*, $NHBz\cdot C_6H_2(NO_2)_2\cdot OH$, is formed by the action on *p*-benzoylaminophenol of a mixture of concentrated sulphuric acid and nitric acid of sp. gr. 1·4 at 7—12°, or of nitric acid of sp. gr. 1·5 at −10—0°, or of nitric acid of sp. gr. 1·34 at 20—26°. It crystallises from acetone in golden leaflets, melts at 263°, and when heated with concentrated sulphuric acid on the water-bath is hydrolysed with formation of *iso*picramic acid. The *acetyl* derivative crystallises in yellowish-brown needles or brown prisms and melts at 180°. When reduced with zinc and hydrochloric acid, 2 : 6-dinitro-4-benzoylaminophenol yields *p*-triaminophenol and benzoic acid.

The action of nitric acid of sp. gr. 1·4 on dibenzoyl-*p*-aminophenol (*a*) in concentrated sulphuric acid at 7—14° leads to the formation of 2 : 6-dinitro-4-benzoylaminophenol, melting at 263° ; (*b*) in a mixture of concentrated sulphuric acid and acetic anhydride at 6—11° leads to the formation of dinitro-*p*-nitrobenzoylaminophenyl nitrobenzoate, melting at 229° ; or (*c*) in a mixture of concentrated sulphuric acid and glacial acetic acid to the formation of 3-nitro-4-benzoylaminophenyl benzoate, melting at 147°. G. Y.

Tetrabromo-*p*-cresol ψ-Bromide. XV. Theodor Zincke and K. Böttcher (*Annalen*, 1905, **343**, 100—129. Compare this vol., i, 172).—This communication is an extension of the research on the same subject previously published (Abstr., 1902, i, 284). The results are in agreement with the views expressed by Auwers (Abstr., 1902, i, 217), and, in consequence, the formulæ previously suggested are now somewhat modified.

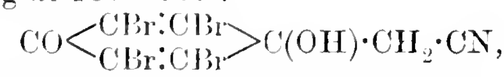
Octabromo-p-*diphenolmethane*, $CH_2(C_6Br_4{\cdot}OH)_2$, prepared by dissolving tetrabromo-*p*-cresol ψ-bromide in 5 per cent. sodium hydroxide or by heating tetrabromo-*p*-hydroxybenzyl alcohol at 200°, crystallises in needles or leaflets melting at 280—281° ; its *acetyl* derivative crystallises in needles melting at 278—279°.

Tetrabromo-p-*hydroxybenzylacetone*, $OH{\cdot}C_6Br_4{\cdot}CH_2{\cdot}CH_2{\cdot}COMe$, prepared from the ψ-bromide by the action of alkali hydroxide in acetone solution, crystallises in colourless needles melting at 175—176° ; its *sodium* salt forms scales and its *acetyl* derivative needles melting at 181—182°. *Ethyl tetrabromo*-p-*hydroxybenzylacetoacetate*,

$$OH{\cdot}C_6Br_4{\cdot}CH_2{\cdot}CHAc{\cdot}CO_2Et,$$

prepared by boiling a mixture of ethyl sodioacetoacetate and tetrabromo-*p*-cresol ψ-bromide in benzene solution, crystallises in needles melting at 117—118°, and is converted into the acetone derivative just described by boiling with a solution of barium hydroxide.

Tetrabromo-p-*hydroxybenzylaniline*, prepared from the tetrabromo-ψ-bromide and aniline (2 molecules), crystallises in needles melting at 120—122°. The corresponding *tetrabromo*-p-*hydroxyphenylacetonitrile*, prepared from the tetrabromo-ψ-bromide and potassium cyanide, crystallises in needles melting at 214—216° ; by dilute sulphuric acid, it is hydrolysed to the corresponding acid, and by nitric acid it is oxidised to a ψ-quinol and oxalic acid. Its *acetyl* derivative forms crystals melting at 183—184°.



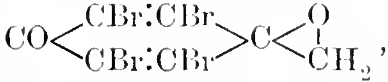
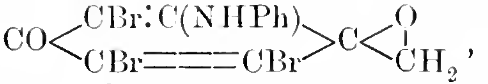
The *quinol*, $CO<\begin{matrix}CBr{:}CBr\\CBr{:}CBr\end{matrix}>C(OH){\cdot}CH_2{\cdot}CN$, prepared from the nitrile, crystallises in yellow needles or prisms melting at 209—211°. *Tetrabromo*-p-*hydroxyphenylacetic acid*, $OH{\cdot}C_6Br_4{\cdot}CH_2{\cdot}CO_2H$, prepared from the nitrile, crystallises in needles melting and decomposing at 265° ; its *acetyl* derivative forms crystals melting at 250—255° ; its *methyl* ester crystallises in needles melting at 220—221°, and forms a sparingly soluble *sodium* derivative and an *acetyl* derivative which crystallises in needles melting at 159°. The *amide*,

$$OH{\cdot}C_6Br_4{\cdot}CH_2{\cdot}CO{\cdot}NH_2,$$

formed as an intermediate product in the preparation of the acid, crystallises in prisms.

*Tetrabromo-*p-*hydroxybenzyl nitrite*, $OH{\cdot}C_6Br_4{\cdot}CH_2{\cdot}ONO$, prepared from the tetrabromo-ψ-bromide and potassium nitrite, crystallises in needles from benzene melting and decomposing at 143°, and when boiled with a methyl-alcoholic solution of sodium hydroxide is converted into tetrabromo-*p*-hydroxybenzyl methyl ether. Its *acetyl* derivative crystallises in leaflets melting at 172—173°.

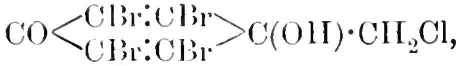
*Tetrabromo-*p-*hydroxybenzyl mercaptan*, $OH{\cdot}C_6Br_4{\cdot}CH_2{\cdot}SH$, prepared by treating the ψ-bromide with alcoholic solution of sodium hydrogen sulphide, crystallises in prisms or needles melting at 152°, and is reconverted into the ψ-bromide by heating with bromine. Its *diacetyl* derivative forms crystals melting at 132—133°. *Tetrabromo-*p-*hydroxybenzyl sulphide*, $(OH{\cdot}C_6Br_4{\cdot}CH_2)_2S$, is formed at the same time as the mercaptan, and is a crystalline powder decomposing at 255°.

The *oxide*,  $\mathrm{CO}<\genfrac{}{}{0pt}{}{\mathrm{CBr{:}CBr}}{\mathrm{CBr{:}CBr}}>\mathrm{C}<\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{CH_2}}$, is obtained from pentabromotolu-ψ-quinol (*loc. cit.*) by regulated treatment of its alcoholic solution with aqueous sodium carbonate; aniline converts the tolu-ψ-quinol into the *compound*  $\mathrm{CO}<\genfrac{}{}{0pt}{}{\mathrm{CBr{:}C(NHPh)}}{\mathrm{CBr{=\!=}CBr}}>\mathrm{C}<\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{CH_2}}$, which crystallises in yellow leaflets melting and decomposing at 209°. When the oxide is heated with a saturated solution of hydrogen bromide in acetic acid, it yields the *compound*  $\mathrm{OH{\cdot}C}\lessdot\genfrac{}{}{0pt}{}{\mathrm{CBr{\cdot}CBr}}{\mathrm{CBr{:}CBr}}\gtrdot\mathrm{C{\cdot}O{\cdot}CH_2Br}$, which crystallises in white needles melting at 150—160°; its *acetyl* derivative, prepared either directly from the compound or by treating the oxide with acetyl bromide and a little concentrated sulphuric acid, crystallises in leaflets melting at 144—145°. When heated with sulphuric acid in acetic acid solution, tetrabromoquinone and tetrabromoquinol are formed.

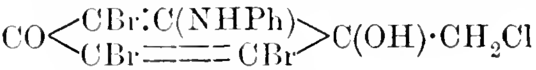
Tetrabromomethylenequinone,  $\mathrm{CO}<\genfrac{}{}{0pt}{}{\mathrm{CBr{:}CBr}}{\mathrm{CBr{:}CBr}}>\mathrm{C{:}CH_2}$ (or a polymeride), is obtained by eliminating hydrogen bromide from the tetrabromo-*p*-cresol ψ-bromide by shaking its benzene solution with anhydrous sodium acetate, and is an amorphous, white powder, which is oxidised to tetrabromobenzoquinone by nitric acid, and is reconverted into the ψ-bromide by hydrogen bromide; by alkalis in acetone solution, it is changed to tetrabromo-*p*-hydroxybenzyl alcohol and tetrabromo-*p*-hydroxybenzylacetone. It yields tetrabromo-*p*-hydroxybenzyl methyl ether with methyl alcohol, and with acetic anhydride, tetrabromo-*p*-acetoxybenzyl acetate. With aniline, it yields two *anilides*, one identical with that obtained by the action of aniline on the ψ-bromide, and a *second*, probably  $\mathrm{CO}<\genfrac{}{}{0pt}{}{\mathrm{CBr{:}CBr}}{\mathrm{CBr{:}CBr}}>\mathrm{CH{\cdot}CH_2{\cdot}NHPh}$, which crystallises in yellow needles melting at 203—205°.

*Tetrabromo-*p-*cresol ψ-chloride*, $C_7H_3OClBr_4$, prepared from tetrabromo-*p*-hydroxybenzyl alcohol and hydrogen chloride, crystallises in needles melting at 174° and resembles the ψ-bromide; its *acetyl* derivative crystallises in needles melting at 180—181°, and when boiled with acetic anhydride is converted into tetrabromo-*p*-acetoxybenzyl acetate. An *isomeride* of the acetyl derivative is obtained when the ψ-chloride is boiled with sodium acetate and acetic acid; it melts at 159—160°.

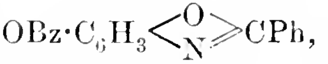
ω-*Chloro*-2 : 3 : 5 : 6-*tetrabromotolu*-ψ-*quinol*,



$$CO<\begin{matrix}CBr:CBr\\CBr:CBr\end{matrix}>C(OH)\cdot CH_2Cl,$$

prepared by heating the ψ-chloride with nitric acid, crystallises in yellow needles melting at 175—176°; its *acetyl* derivative crystallises in needles melting at 154—155°; both are converted into the oxide above described by treatment with alkalis. Aniline converts the tolu-ψ-quinol into an *anilide*,  $CO<\begin{matrix}CBr:C(NHPh)\\CBr\!=\!=\!=\!=CBr\end{matrix}>C(OH)\cdot CH_2Cl$ or  $CO<\begin{matrix}C(NHPh):CBr\\CBr\!=\!=\!=\!=CBr\end{matrix}>C(OH)\cdot CH_2Cl$, which crystallises in yellowish-red needles melting at 180—181°. K. J. P. O.

Derivatives of the Volatile Nitroresorcinol. HUGO KAUFFMANN and ERWIN DE PAY (*Ber.*, 1906, **39**, 323—328. Compare Abstr., 1904, i, 157).—The *hydrochloride* of 2-aminoresorcinol, $C_6H_7O_2N,HCl$, is prepared by reducing 2-nitroresorcinol with tin and hydrochloric acid at 85°, saturating the cooled reaction-product with hydrogen chloride, and recrystallising the precipitate from concentrated hydrochloric acid; it is obtained in white, well-formed crystals. The free *base* is unstable and cannot be isolated; it reduces ammoniacal silver and Fehling's solutions, and may be used as a photographic developer. The action of sodium nitrite on the cooled solution of the hydrochloride leads to the formation of a *nitroso*-derivative of resorcinol diazonium anhydride, $C_6H_3O_3N_3$, which crystallises from acetone in greyish-green needles, begins to decompose at 176°, and explodes at 195°; it dissolves in aqueous alkali hydroxides to form red solutions, from which it is reprecipitated unchanged on acidification.

Dibenzoyl-2-nitroresorcinol, formed from 2-nitroresorcinol by the action of benzoyl chloride and sodium carbonate, crystallises from alcohol in yellowish-white needles and melts at 140° (compare Pechmann and Obermiller, Abstr., 1901, i, 336). When reduced with iron powder and glacial acetic acid, it yields 2-*benzoylaminoresorcinol*, $C_6H_3(OH)_2\cdot NHBz$, which crystallises from alcohol in nacreous leaflets, melts at 187°, and is soluble in aqueous alkali hydroxides, and 3-*benzoxy*-1-*phenylbenzoxazole*,  $OBz\cdot C_6H_3<\begin{matrix}O\\N\end{matrix}>CPh$, which crystallises from light petroleum in white leaflets, melts at 140°, and is insoluble in aqueous alkali hydroxides.

When treated with sodium nitrite and dilute hydrochloric acid, 2-benzoylaminoresorcinol yields a *nitroso*-derivative, $C_{13}H_{10}O_4N_2$, which crystallises in red needles, melts at 208°, and dissolves without decomposing in aqueous alkali hydroxides.

2-Nitroresorcinol couples with 1 mol. of benzenediazonium chloride in alkaline solution to form the *mono-azo*-dye, $C_{12}H_9O_4N_3$, which crystallises from glacial acetic acid in dark red needles, melts at 171°, and is soluble in aqueous alkali hydroxides, forming orange-red solutions.

The *azo*-dye, $C_{18}H_{13}O_4N_5$, formed by coupling 2-nitroresorcinol with 2 mols. of benzenediazonium chloride, crystallises in dark red needles and commences to decompose at 260°; it dissolves in dilute alkali hydroxides to form violet-red solutions.

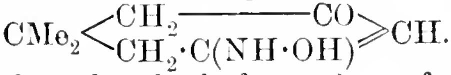
The nitro-azo-dyes were compared spectroscopically with the corresponding resorcinol dyes in sulphuric acid and in acetone solution containing $4/3 \times 10^{-3}$ mol. per litre. All the solutions exhibit absorption at the violet end of the spectrum only; with the nitro-dyes, in long layers (20 cm.), the absorption extends further into the yellow than with the resorcinol derivatives; the difference is greatest with the mono-azo-dyes in acetone solution. The introduction of a nitro-group into a resorcinol azo-dye is accompanied by a slight increase in the depth of colour.

2-Nitroresorcinol interacts with benzenediazonium chloride in acid-alcoholic solution to form a *substance*, $C_{12}H_9O_4N_3$, which crystallises from glacial acetic acid in light red needles and melts at 175—176°.

G. Y.

Action of Hydroxylamine on Dimethyldihydroresorcin.

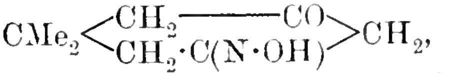
W. Gittel (*Chem. Centr.*, 1906, i, 33—35; from *Zeit. für Naturwiss*, **77**, 145—173).—Dimethyldihydroresorcin yields a crystalline and an amorphous oxime, both of which have the same molecular weight. Since the amorphous form, which is stable in the presence of acids, cannot be converted into a dioxime, it would appear to have the constitution of a hydroxamic acid,



$CMe_2<\begin{array}{l}CH_2\text{———}CO\\CH_2\cdot C(NH\cdot OH)\end{array}\!\!>CH$.

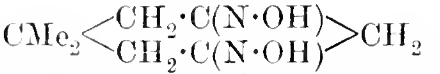
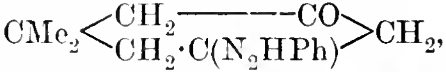
On the other hand, however, the fact that both forms have faintly acid properties renders it more probable that they are stereoisomerides. The anilino-derivative of dimethyldihydroresorcin only exists in one form, which resembles that of the amorphous oxime; it neither yields a dianilino-derivative nor a dioxime.

The amorphous *oxime*,



$CMe_2<\begin{array}{l}CH_2\text{———}CO\\CH_2\cdot C(N\cdot OH)\end{array}\!\!>CH_2$, prepared by the action of hydroxylamine hydrochloride on dimethyldihydroresorcin, separates from ether in the form of a brittle mass which is soluble in alcohol, chloroform or benzene, somewhat soluble in a large quantity of a solution of sodium carbonate, and very readily so in potassium hydroxide, acetic acid, or dilute hydrochloric acid; it gives a reddish-brown coloration with ferric chloride and reduces Fehling's solution on warming. It neither forms an oxime nor yields crystalline compounds with acetic anhydride in presence of hydrogen chloride or concentrated sulphuric acid. The *hydrochloride* of the crystalline *oxime*, $C_{18}H_{14}O_2NCl$, obtained by allowing the oxime to remain with concentrated hydrochloric acid for six days, forms large crystals, melts about 152°, and is readily soluble in alcohol or water, but insoluble in ether. It is not readily attacked by concentrated hydrochloric acid; its aqueous solution gives a yellow precipitate with formaldehyde which melts at 78—80°.

The crystalline *oxime* forms a white mass which melts at 115° and is soluble in hot water, alkali hydroxides, hydrochloric acid, or acetic acid; it reduces alkaline solutions of copper or ammoniacal solutions of silver on warming, and gives a reddish-brown coloration with ferric chloride, but is not attacked by warm acetic anhydride. By the action of semicarbazide in alkaline solution, an amorphous, brick-red substance is formed which is soluble in hydrochloric acid and potassium hydroxide, forming yellow and red solutions respectively.

The *dioxime*,  $CMe_2<\begin{matrix}CH_2\cdot C(N\cdot OH)\\CH_2\cdot C(N\cdot OH)\end{matrix}>CH_2$ (compare Vorländer, Abstr., 1897, i, 273), prepared from the crystalline oxime or from dimethyldihydroresorcin, is soluble in alkali hydroxides, hydrochloric acid, or acetic acid, but is insoluble in a solution of sodium carbonate; it reduces an alkaline solution of copper, and with ferric chloride gives a faint brown coloration which gradually becomes darker. Benzoyl chloride and acetic anhydride yield amorphous products. The *ethyl* derivative, prepared by the action of ethyl iodide and sodium on the dioxime, separates as a resin which is soluble in hydrochloric or acetic acid, less so in solutions of alkali hydroxides, and insoluble in sodium carbonate. The *hydrochloride*, $C_8H_{15}O_2N_2Cl$, forms highly refractive, colourless crystals, which are probably monoclinic and are readily soluble in alcohol; it becomes darker at 175° and decomposes at 185° without melting. The *phenylhydrazone*,  $CMe_2<\begin{matrix}CH_2\text{———}CO\\CH_2\cdot C(N_2HPh)\end{matrix}>CH_2$, is a hygroscopic, bright yellow powder, which on exposure to air becomes flesh-coloured to orange-red and melts and decomposes at 158°. It is soluble in alcohol or acetone, sparingly so in chloroform, and insoluble in ethyl acetate, ether, carbon disulphide, light petroleum, benzene, hydrochloric acid, or potassium hydroxide and gives a slight brown coloration with ferric chloride. The alcoholic solution forms a deep blue coloration with dilute nitric acid and becomes green when warmed with dilute sulphuric acid. When concentrated hydrochloric acid is poured over the phenylhydrazone, a white substance is obtained which becomes dark at 170° and melts at 181°. When treated with dry hydrogen chloride, the phenylhydrazone becomes emerald-green, but by the action of the gas on the powder suspended in chloroform or ethyl acetate, the liquid changes to bluish-green, bright blue, and finally to greyish-blue or violet, and a *compound*, $C_{23}H_{13}N_5Cl$ (?), is formed, the phenylhydrazone being partially decomposed and dimethyldihydroresorcin regenerated; the compound forms a white powder which, on exposure to the atmosphere, partially becomes blue. By the action of concentrated alkaline solutions, orange-red flakes are formed, which rapidly become scarlet and dissolve in alcohol, forming an orange-red solution. When the solution is treated with hydrochloric acid, it becomes green, then blue, and finally olive-green, and an amorphous, flocculent precipitate is formed; ammonia restores the orange-red colour of the solution. By the action of dilute nitric acid, a blackish-brown dye is formed, and when treated with a small quantity of concentrated sulphuric acid a product is obtained which is possibly a sulphonic acid. *Anilinodimethyldihydroresorcin*,

$$\mathrm{CMe_2}<\begin{matrix}\mathrm{CH_2}\text{———}\mathrm{CO}\\ \mathrm{CH_2\cdot C(NHPh)}\end{matrix}>\mathrm{CH},$$

separates from its alcoholic solution in white crystals, melts at 181°, is readily soluble in alcohol, chloroform, or glacial acetic acid, less so in hydrochloric acid, sparingly soluble in acetone, ether, or light petroleum, and insoluble in potassium hydroxide; it gives a wine-red coloration with ferric chloride and a blackish-brown dye is formed by the action of nitrous acid.

The *hydrochloride*, $C_{14}H_{18}ONCl$, prepared by passing hydrogen chloride into a solution of the anilino-derivative in chloroform, is a white substance which crystallises from alcohol, sinters at 205°, and melts at 214—217°. The *acetoxy*-derivative separates from ethyl acetate in the form of a yellow, crystalline mass which sinters at 57° and melts at 62°; it is readily soluble in alcohol, ether, chloroform, or light petroleum, less so in hydrochloric acid in presence of alcohol, and only sparingly so in potassium hydroxide. It does not give a reaction with ferric chloride, but is decomposed by concentrated hydrochloric acid at the ordinary temperature.

The o-*toluidino*-derivative, $C_{15}H_{19}ON$, crystallises from aqueous alcohol in slender needles, melts at 135°, and gives a reddish-brown coloration with ferric chloride. The *hydrochloride*, $C_{15}H_{20}ONCl$, separates from the alcoholic solution in white crystals, sinters at 204°, and melts at 208°; when treated with water, it becomes yellow and is apparently decomposed. The p-*toluidino*-derivative crystallises from alcohol and melts at 202°; the *hydrochloride* forms strongly etched crystals, is soluble in alcohol, sinters at 197°, and becomes dark and melts at 206—210°. The *a-naphthylamino*-derivative separates from the alcoholic solution in a greyish-white, crystalline form, melts at 175°, and gives a blood-red coloration with ferric chloride; the *hydrochloride* forms rectangular crystals, melts at 226—230°, is soluble in alcohol or chloroform, insoluble in ether, and gives a reddish-brown coloration with ferric chloride.

It is probable that phenyldihydroresorcin also forms two isomeric oximes. The greasy, yellow substance which is obtained together with a resinous product by the action of hydroxylamine hydrochloride on phenyldihydroresorcin melts at 95—103°, is soluble in alcohol (compare Vorländer, *loc. cit.*), and reduces Fehling's solution on warming; its solution in hydrochloric acid is yellow and in alkali red. The main product of the reaction, however, forms a white, resinous mass which, on exposure to the atmosphere, becomes successively yellow, orange, and brown. With glacial acetic acid, it yields a small quantity of a substance which melts at 185—187° and is readily soluble in potassium hydroxide, but only sparingly so in hydrochloric acid or a solution of sodium carbonate; by the action of acetic anhydride and dry hydrogen chloride, a portion probably is converted into the crystalline oxime which melts at 79—82°. E. W. W.

Action of Bromine and Chlorine on Phenols. Substitution Products. ψ-Bromides and ψ-Chlorides. XIV. Action of Bromine on *p*-Diphenoldimethylmethane. ψ-Bromides and Quinones of *p-iso*Propylphenol. Theodor Zincke and Max Grüters (*Annalen*, 1905, **343**, 75—99. Compare Abstr., 1904, i, 41, 401, 1005; 1905, i, 55, 342).—The ψ-bromide of *iso*propylphenol is obtained from diphenoldimethylmethane, which readily decomposes into phenol and *iso*propylphenol.

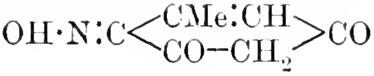
p-*Diphenoldimethylmethane*, $CMe_2(C_6H_4{\cdot}OH)_2$, is prepared by warming a mixture of phenol, acetone, and concentrated hydrochloric acid for three days and then treating the mixture with 40 per cent. acetic acid; it crystallises in colourless needles or prisms melting at 152—153°.

3 : 5 : 3′ : 5′-*Tetrabromo*-p-*diphenoldimethylmethane*, $CMe_2(C_6H_2Br_2{\cdot}OH)_2$, prepared by the action of bromine in acetic acid on the compound last mentioned, crystallises in prisms or spikes melting at 162—163° and is soluble in alkali hydroxides without decomposition; the *acetyl* derivative crystallises in needles melting at 169—170°. When a solution of the tetrabromide in acetic acid is treated with solid sodium nitrite at the ordinary temperature, two atoms of bromine are replaced by nitro-groups, a 3 : 3′-*dibromo*-5 : 5′-*dinitro*-p-*diphenoldimethylmethane*, $C_{15}H_{12}O_6N_2Br_2$, being formed; it crystallises in yellow needles melting at 176°, and yields red ammonium and alkali salts; its *acetyl* derivative crystallises in yellow needles melting at 196—197°.

ψ-p-*Tribromo*iso*propyltetrabromophenol* (ψ-*heptabromo*-p-iso*propylphenol*),  $CO<\begin{smallmatrix}CBr{:}CBr\\CBr{:}CBr\end{smallmatrix}>CH{\cdot}CBrMe{\cdot}CHBr_2$, is formed together with tribromophenol when the tetrabromide described above is heated with bromine at 100°; it crystallises in prisms melting and decomposing at 182—183°, and when treated with acetone is immediately converted into hexabromoquinone; with acetic anhydride at the ordinary temperature, a heptabromoacetyl derivative is produced, and at a higher temperature the pentabromoacetyl derivative. *Acetylheptabromo*-p-iso*propylphenol*, $C_{11}H_7O_2Br_7$, crystallises in colourless needles melting at 166°, and by alcoholic potash is converted into hexabromo*iso*propenylphenol.

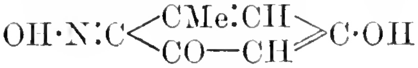
p-*Dibromo*iso*propylidenetetrabromoquinone* (*hexabromo*iso*propylidenequinone*),  $CO<\begin{smallmatrix}CBr{:}CBr\\CBr{:}CBr\end{smallmatrix}>C{:}CMe{\cdot}CHBr_2$, is prepared by slowly adding water to an acetone solution of the heptabromide, and crystallises in yellow needles or prisms melting at 185°. When treated with acetic anhydride in the presence of sulphuric acid at the ordinary temperature, it is converted into p-α-*dibromo*-β-*acetoxy*iso*propyltetrabromophenyl acetate*, $OAc{\cdot}C_6Br_4{\cdot}CMe(OAc){\cdot}CHBr_2$, which crystallises in prisms melting at 144—145°; when hydrolysed, it yields not the corresponding phenol but hexabromo*iso*propenylphenol. The corresponding *phenolalcohol* is formed in small quantity when the quinone is treated with sulphuric acid in acetic acid solution, and crystallises in needles melting at 114—117°. It readily loses water, forming the propenyl derivative. p-*Dibromo*iso*propenyltetrabromophenol* (*hexabromo*-p-iso*propylenephenol*), $OH\cdot C_6Br_4\cdot CMe\dot{:}CBr_2$, formed by hydrolysing the heptabromo-acetate in alcoholic solution or by reduction of the quinone with an alkaline solution of stannous chloride, crystallises in colourless needles melting at 134—135°; it yields a sparingly soluble *sodium* salt, and is again converted into the ψ-heptabromide by hydrobromic acid in acetic acid solution. The *acetyl* derivative crystallises in monoclinic prisms melting at 114—115°. p-*Bromo*iso*propenyltetrabromophenol* (*pentabromo*-p-iso*propylenephenol*), $OH\cdot C_6Br_4\cdot CMe\dot{:}CHBr$, prepared from the hexabromo*iso*propylidenequinone by keeping its acetone solution or by reducing the hexabromoquinone with stannous chloride in acetic acid solution, crystallises in needles melting at 88—89°; it yields a crystalline *sodium* salt, is converted by bromine into the heptabromo-ψ-bromide, and with nitric acid yields a crystalline product. Its *acetyl* derivative crystallises in monoclinic prisms melting at 126—127°, and is formed when the heptabromo-ψ-bromide or hexabromoquinone is boiled with acetic anhydride. K. J. P. O.

The Isomeric Nitroso-orcinols. ARTHUR HANTZSCH and C. H. SLUITER (*Ber.*, 1906, **39**, 162—166. Compare Henrich, Abstr., 1900, i, 163, 436; 1901, i, 464; Hantzsch and Voegelen, 1902, i, 260).—Henrich's yellow modification of nitroso-orcinol crystallises from alcohol in yellowish-brown needles, decomposes at 163°, and has $K = 0{\cdot}037$. Its aqueous solution has an orange-yellow colour. The red modification crystallises from boiling benzene and has a transition temperature 124—125° and $K = 0{\cdot}051$. Its aqueous solutions are orange-red in colour, and are perfectly stable when the compounds are pure, otherwise there is a tendency to the formation of an equilibrium mixture of the two; the point of equilibrium is not reached, however, even at the end of several weeks. The addition of alcohol immediately causes the equilibrium to be attained, solutions of both substances then have the same conductivity. Raising the temperature to 50° does not produce the change of the one form into the other. Both modifications yield the same potassium or ammonium salt. These facts are in harmony with Henrich's constitutional formulæ,



$$\mathrm{OH{\cdot}N{\dot{:}}C}<\begin{matrix}\mathrm{CMe{\dot{:}}CH}\\ \mathrm{CO{-}CH_2}\end{matrix}>\mathrm{CO}$$

Red.



$$\mathrm{OH{\cdot}N{\dot{:}}C}<\begin{matrix}\mathrm{CMe{\dot{:}}CH}\\ \mathrm{CO{-}CH}\end{matrix}\geqslant\mathrm{C{\cdot}OH}$$

Yellow.

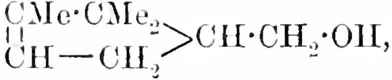
J. J. S.

Replacement of the Acetyl Group by Methoxyl under the Action of Diazomethane. JOSEF HERZIG and J. TICHATSCHEK (*Ber.*, 1906, **39**, 268).—When triacetylpyrogallol is exposed to the action of diazomethane at the ordinary temperature for forty-eight hours, the product is found to contain 10·4 per cent. of methoxyl. The acetyl derivative of phloroglucinol diethyl ether is under similar conditions converted almost completely into phloroglucinol methyl diethyl ether. W. A. D.

Peculiar Behaviour of Hexabromodiresorcinol in Alkaline Solution. HEINRICH BECHHOLD (*Zeit. Elektrochem.*, 1905, **11**, 845—846).—When dissolved in less than 2·5 molecules of alkali hexabromodiresorcinol oxidises in presence of the atmosphere to a blue colouring matter, when more alkali is used the solution remains unchanged. The different ionisation in the two cases is suggested as the cause of the difference. T. E.

α- and β-Campholytic Alcohols. GUSTAVE BLANC (*Compt. rend.*, 1906, **142**, 283—285. Compare Abstr., 1900, i, 581; 1905, i, 11).—*Dihydro-β-campholyl alcohol*, $C_8H_{15}\cdot CH_2\cdot OH$, obtained by reducing ethyl β-campholytate or the corresponding amide with alcohol and sodium is a colourless, viscous liquid which boils at 198°, has a sp. gr. 0·9056 at 21·5°/4°, and n_D 1·4641 at 21·5°. The *pyruvate*, $C_8H_{15}\cdot CH_2\cdot O\cdot CO\cdot COMe$, is a mobile liquid boiling at 140—142° under 17 mm. pressure and has an agreeable penetrating odour; the *semicarbazone* crystallises from alcohol and melts at 158°; the *chloride*, $C_8H_{15}\cdot CH_2Cl$, boils at 175°.

α-Campholyl alcohol,



$$\begin{array}{l}CMe\cdot CMe_2\\ \| \\ CH—CH_2\end{array}>CH\cdot CH_2\cdot OH$$

obtained by reducing the ethyl ester or the amide of α-campholytic acid with alcohol and sodium, is a viscous liquid boiling at 200° and having a sp. gr. 0·9273 at 23°/4° and n_D 1·4762 at 23°; the *pyruvate*, $C_8H_{13}\cdot CH_2\cdot O\cdot CO\cdot COMe$, boils at 143—144° under 17 mm. pressure; the *semicarbazone* melts at 137°. M. A. W.

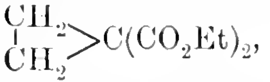
Cholesterol. V. ADOLF WINDAUS (*Ber.*, 1906, **39**, 518—523. Compare Abstr., 1904, i, 49, 667, 1010; 1905, i, 128; Diels and Abderhalden, Abstr., 1904, i, 880).—Chromic acid and acetic acid at 70°, or sulphuric acid and potassium permanganate in the cold, oxidise dibromocholesterol to dibromocholestenone, which is reduced to cholestenone by zinc dust and acetic acid. Cholestenone gives a rose-red coloration with concentrated nitric acid; when heated on the water-bath with a mixture of equal volumes of acetic acid and nitric acid of sp. gr. 1·4, it yields a *nitro*-derivative, probably $C_{27}H_{41}O_6N_3$, which crystallises from acetone in glassy leaflets melting at 194—195°. Cholestenone is stable towards a 3 per cent. alcoholic solution of hydrogen chloride, a 10 per cent. alcoholic solution of potassium hydroxide, or towards diethylamine; when heated at 210—220° with piperidine, it yields a *substance*, $C_{32}H_{51}N$ or $C_{32}H_{53}N$, which forms large crystals melting at 159°.

Cholestenone is probably not an αβ-unsaturated ketone, since its reduction by sodium amalgam in 95 per cent. alcoholic solution gives an unsaturated *pinacone*, $C_{54}H_{86}O_2$ or $C_{54}H_{90}O_2$, crystallising in needles which sinter and melt at 221° (compare Harries, Abstr., 1904, i, 427). With acetic anhydride, the pinacone yields a *hydrocarbon*, $C_{54}H_{82}$ or $C_{54}H_{86}$ (compare Lieben, Abstr., 1905, i, 167). The same hydrocarbon seems to be produced by the reduction of cholestenone with zinc dust and alcoholic hydrogen chloride, and in the reduction of dibromocholestenone. C. S.

Ergosterol. D. OTTOLENGHI (*Atti R. Accad. Lincei*, 1905, [v], **14**, ii, 697—705. See this vol., ii, 202).

Action of Ethylene Dibromide on Ethyl Sodiocyanoacetate. Léonce Barthe (*Bull. Soc. chim.*, 1906, [iii], **35**, 40—47. Compare Abstr., 1894, i, 492).—The author has repeated the work of Carpenter and Perkin (Trans., 1899, **75**, 924) and generally confirmed their observations.

Ethyl cyanotrimethylenecarboxylate,  $\left.\begin{array}{l}CH_2\\ CH_2\end{array}\right>C(CN)\cdot CO_2Et$, boils at 137° under 80 mm. pressure and is hydrolysed by hydrogen chloride in presence of alcohol to *ethyl trimethylenedicarboxylate*,



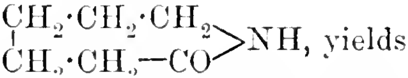
$$\left.\begin{array}{l}CH_2\\ CH_2\end{array}\right>C(CO_2Et)_2,$$

which is a colourless, oily liquid and boils at 130° under 70 mm. pressure. The author cannot confirm Carpenter and Perkin's statement that ethyl cyanotrimethylenecarboxylate is hydrolysed by potassium hydroxide in alcohol to the corresponding cyano-acid, but a small yield of the latter was obtained by adding metallic sodium to a solution of the ester in alcohol. The *magnesium* salt crystallises with H_2O.

The crystalline accessory substance melting at 119° obtained by Carpenter and Perkin (*loc. cit.*), and which, since it yielded adipic acid on hydrolysis, they regarded as ethyl $\alpha\delta$-dicyanovalerate, furnished malonic acid when hydrolysed with hydrochloric acid. Hydrolysis carried out with other agents gave the present author inconclusive results.

T. A. H.

Terpenes and Ethereal Oils. LXXIV. *cyclo*Hexanone. Otto Wallach (*Annalen*, 1905, **343**, 40—53).—This paper contains in part an account of work previously published, together with corrections and amplifications.

*cyclo*Hexanone*iso*oxime,  $\left.\begin{array}{l}CH_2\cdot CH_2\cdot CH_2\\ CH_2\cdot CH_2-CO\end{array}\right>NH$, yields on hydrolysis ϵ-aminohexoic acid, $NH_2\cdot CH_2\cdot[CH_2]_4\cdot CO_2H$, which is oxidised by alkaline permanganate to normal adipic acid. Suberone*iso*oxime similarly yields ζ-aminoheptoic acid, which is oxidised to pimelic acid.

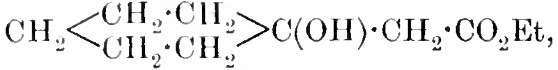
On reducing the hexanone*iso*oxime with sodium in amyl alcohol solution, unsaturated fatty acids are mainly formed together with cyclo*hexylamine* (not, as was expected, hexamethyleneimine, Abstr., 1905, i, 826), $C_6H_{11}\cdot NH_2$, which is an oil boiling at 135—138° and having a sp. gr. 0·863 and n_D 1·4575 at 24°. The *hydrochloride* melts at 203—204°, the *benzoyl* derivative at 149°, the *carbamide* at 195—196°, and the *methiodide* at 260°. The amine is probably formed from the hexamethyleneimine by fission into an intermediary acyclic compound, which by renewed ring formation passes into *cyclo*hexylamine. Some hexamethyleneimine seems to be present in the more volatile fractions.

When ϵ-aminohexoic acid is oxidised with nitric acid, ϵ-hydroxyhexoic acid is formed. The latter loses water, forming a mixture of Δ^{δ}- and Δ^{γ}-hexenoic acids.

Tetrahydrobenzene forms a nitrosochloride when a solution of the hydrocarbon in acetic acid is treated successively with ethyl nitrite and concentrated hydrochloric acid. The nitrosochloride is an unusually stable substance.

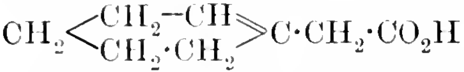
1-Methyl*cyclo*hexane-2-one is prepared from Δ^1-tetrahydrotoluene which can now be easily obtained by Grignard's method from methyl iodide and *cyclo*hexanone; this reaction first yields 1-methyl*cyclo*hexane-1-ol. The latter is then dehydrated.

[With EDUARD ISAAC.]—*Ethyl* cyclo*hexanolacetate*,



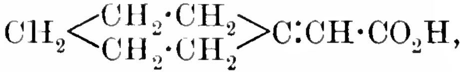
$$CH_2<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>C(OH)\cdot CH_2\cdot CO_2Et,$$

is prepared from *cyclo*hexanone and ethyl bromoacetate by the agency of magnesium. It passes readily by loss of water into ethyl *cyclo*hexeneacetate, which on hydrolysis yields *cyclo*hexeneacetic acid,



$$CH_2<\begin{matrix}CH_2-CH\\CH_2\cdot CH_2\end{matrix}\gg C\cdot CH_2\cdot CO_2H$$

or



$$CH_2<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>C:CH\cdot CO_2H,$$

melting at 37—38° and boiling at 140° under 12 mm. pressure. It takes up bromine in ethereal solution, giving dibromo*cyclo*hexaneacetic acid, $C_8H_{12}O_2Br_2$, which crystallises in prisms melting at 119—120° and is converted into an oil on treatment with alkali carbonates.

When *cyclo*hexeneacetic acid is oxidised at 0° by permanganate, a *cyclo*hexanone is not formed, but a compound with seven carbon atoms which is not an aldehyde. K. J. P. O.

5-Bromo-2-aminobenzoic Acid and Certain Derivatives. MARSTON T. BOGERT and WILLIAM F. HAND (*J. Amer. Chem. Soc.*, 1905, **27**, 1476—1484).—5-Bromo-2-acetylaminobenzoic acid (5-bromoacetylanthranilic acid) (Jackson, Abstr., 1881, 735) was prepared by the direct bromination of acetylanthranilic acid, by the oxidation of 5-bromo-*o*-acetyltoluidine, and by the hydrolysis of 5-bromoacetylanthranil; it crystallises in transparent, six-sided, microscopic prisms and melts at 222—223° (corr.). The *barium* salt was prepared. 5-Bromo-2-aminobenzoic acid melts at 219—220° (corr.), and not at 211·5—212° as stated by Alt (Abstr., 1889, 987); its *hydrochloride* and *barium* salt are described. 5-*Bromoacetylanthranil* crystallises in colourless scales and melts at 131° (corr.). 5-*Bromo-2-acetylaminobenzonitrile*, obtained by the action of bromine on acetylaminobenzonitrile, forms six-sided prisms, melts at 158° (corr.), and is easily soluble in alcohol, acetone, ethyl acetate, hot benzene, or chloroform, and sparingly so in water.

E. G.

Stereoisomeric Cinnamic Acids. EMIL ERLENMEYER, jun. (*Ber.*, 1906, **39**, 285—292. Compare Abstr., 1905, i, 892; this vol., i, 21).—Synthetically prepared cinnamic acid gives with brucine in alcoholic solution three different brucine salts of the same composition, melting at 135°, 113°, and 107° respectively. Cinnamic acid from storax gives only the brucine salt melting at 135°, which in 1 per cent. alcoholic solution is optically inactive. The salt melting at 113° in 1 per cent. alcoholic solution has $[\alpha]_D - 12·5°$. Cinnamic acid from storax has a solubility in absolute alcohol of 12·72 grams per 100 c.c., whilst synthetical cinnamic acid has a somewhat greater solubility, namely, 13·88 grams per 100 c.c.; the two acids show a strikingly different behaviour when recrystallised from alcohol. Cinnamic acid from storax is converted into synthetical cinnamic acid when heated for ten hours with concentrated sodium hydroxide. All three of the brucine salts separated from alcohol give, on crystallisation from benzene, the same product, $C_9H_8O_2,C_{23}H_{26}O_4Na,C_6H_6$, melting at 92—93°; but on volatilising the benzene of crystallisation at 70—80°, the differences between the salts reappear.

On combining synthetical cinnamic acid with *l-iso*diphenyloxyethylamine and crystallising from alcohol, two different *salts* containing alcohol of crystallisation are obtained; the more soluble *salt* melts, when the alcohol has been expelled, at 128°, and in 1 per cent. alcoholic solution gives $[\alpha]_D - 46\cdot5^\circ$; the less soluble *salt* melts at 136—137° and has $[\alpha]_D - 63\cdot5^\circ$. From *d-iso*diphenyloxyethylamine and synthetical cinnamic acid, two analogous *salts* are obtained, melting at 136° and 128° with nearly corresponding dextro-rotations.

With storax cinnamic acid, *l-iso*diphenyloxyethylamine gives only a *salt* containing 2EtOH, which, when dried in the air, melts at 75—80°, and when dried at 80° melts at 128°; in 1 per cent. alcoholic solution it has $[\alpha]_D - 44\cdot4^\circ$. With the same acid, *d-iso*diphenyloxyethylamine gives a *salt* melting at 130—132° when dried in the air, and at 136° when dried at 80°; in 1 per cent. alcoholic solution, it has $[\alpha]_D + 64^\circ$.

Storax cinnamic acid thus seems to be a component of synthetical cinnamic acid. The cases which the author has dealt with seem to point to the existence of a new class of stereoisomerism; its nature is briefly discussed. W. A. D.

Action of Pyridine on Salicyl Chlorides. RICHARD B. EARLE and H. LOUIS JACKSON (*J. Amer. Chem. Soc.*, 1906, **28**, 104—114).—When pyridine is added to a solution of 3 : 5-dichlorosalicyl chloride, *dichlorosalicylide*, $(C_7H_2O_2Cl_2)_4$, corresponding with the salicylide described by Anschütz (Abstr., 1893, i, 165), is produced, which is insoluble in the usual solvents but is soluble in hot anisole or hot nitrobenzene, separates from the latter solvent in short, prismatic crystals, melts and decomposes at about 330°, and is very stable; it is very slowly attacked by aqueous potassium hydroxide, but is readily hydrolysed by alcoholic potassium hydroxide. The molecular weight was determined in boiling anisole; the constant K for this solvent was found to be 4502 (calculated, $K = 4595$).

3 : 5-*Dibromosalicyl chloride*, obtained by the action of phosphorus pentachloride on 3 : 5-dibromosalicylic acid, crystallises from light petroleum and melts at 83—85°. When pyridine is added to a solution of the chloride in light petroleum, cooled to −6°, a precipitate is produced which is probably a mixture of substances. On adding pyridine to a solution of the chloride in acetone, cooled to −16°, a precipitate is obtained which has no definite melting point and is easily soluble in chloroform or benzene; a cryoscopic determination of the molecular weight in benzene solution indicated that the substance was a *heptasalicylide*, but it is possible that its complexity changes on solution. The lack of a definite melting point suggested that changes take place in the molecular weight of the substance, and its behaviour on heating was therefore studied by means of a dilatometer; it was

found that the substance behaves normally from 75° to 110°, contracts slowly at a constant rate from 110° to 170°, and expands at a rapidly increasing rate from 170° to 200°.

It was observed that during the action of pyridine on each chloride the solution at first became bright yellow, but rapidly faded, the duration of the colour varying with different solvents; a table is given recording the number of seconds during which the colour lasted in various solvents. The colour remained longest in a xylene solution, lasting in this case for about a minute.

On adding organic bases to the coloured solution, colourless precipitates are produced which are at present under investigation.

E. G.

Action of Zinc on a Mixture of Cinnamaldehyde and Ethyl α-Bromopropionate. L. Baidakowsky (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 896—902).—The action of a freshly-prepared zinc-copper couple on a mixture of cinnamaldehyde and ethyl α-bromopropionate in an atmosphere of carbon dioxide proceeds according to the equations: (1) $CHMeBr\cdot CO_2Et + Zn = BrZn\cdot CHMe\cdot CO_2Et$; (2) $CHPh{:}CH\cdot CHO + BrZn\cdot CHMe\cdot CO_2Et = CHPh{:}CH\cdot CH(OZnBr)\cdot CHMe\cdot CO_2Et$, which is decomposed by water, giving

$$ZnBr(OH) + EtOH + CHPh{:}CH\cdot CH(OH)\cdot CHMe\cdot CO_2Et.$$

This ester could not be distilled unchanged, and on hydrolysis with 10 per cent. potassium hydroxide or sulphuric acid solution it yields cinnamenylcrotonic acid, $CHPh{:}CH\cdot CH{:}CMe\cdot CO_2H$. If, however, the ester is hydrolysed with cold 5 per cent. barium hydroxide solution, the *barium* salt, $Ba(C_{12}H_{13}O_3)_2,2\frac{1}{2}H_2O$, is obtained as silvery leaflets and yields the *acid*, $C_{12}H_{14}O_3$, in a syrupy form; on boiling the latter with 10 per cent. sulphuric acid solution, it yields a lactone, cinnamenylcrotonic acid, and the unsaturated hydrocarbon, $CHPh{:}CH\cdot CH{:}CHMe$, isolated by Markownikoff (Abstr., 1886, 1015) from Caucasian naphtha.

Cinnamenylcrotonic acid combines with bromine (4 atoms) giving a *compound* which melts and decomposes at about 130° and is readily soluble in alcohol, ether, or benzene, and slightly so in light petroleum.

T. H. P.

Action of Zinc on a Mixture of Salicylaldehyde and Ethyl α-Bromopropionate. Synthesis of α-Methylcoumarin. L. Baidakowsky (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 902—905).—The action of zinc or of a zinc-copper couple on a mixture of salicylaldehyde and ethyl α-bromopropionate should give the ester,

$$OH\cdot C_6H_4\cdot CHMe\cdot CO_2H,$$

but the ester obtained could not be purified as it decomposed on distillation, giving salicylaldehyde and α-methylcoumarin. T. H. P.

Preparation and Properties of β-Cumenyl-α-ethylhydracrylic Acid. A. Kalischeff (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 905—910).—The action of zinc on a mixture of cuminaldehyde and ethyl α-bromobutyrate yields ethyl β-cumenyl-α-ethylhydracrylate, which, on hydrolysis with sodium hydroxide and decomposition of the sodium salt with dilute mineral acid, yields *β-cumenyl-α-ethylhydracrylic acid*, $C_3H_7 \cdot C_6H_4 \cdot CH(OH) \cdot CHEt \cdot CO_2H$, in two modifications, one soluble and the other insoluble in light petroleum. The latter separates from benzene or aqueous alcohol in small crystals melting at 124·5—125·5°; its *sodium*, *barium* ($4H_2O$), *calcium* ($4H_2O$), and *silver* salts were prepared and analysed. On distillation with dilute sulphuric acid, this acid loses water and carbon dioxide, yielding *iso*propylbutenylbenzene, $C_3H_7 \cdot C_6H_4 \cdot CH\colon CHEt$. T. H. P.

Carboxylation of Phenols by means of Carbon Dioxide. II. β-Naphthol-1-carboxylic Acid. Sijbe Tijmstra, jun., and B. G. Eggink (*Ber.*, 1906, **39**, 14—16. Compare Abstr., 1905, i, 439).—A modified method is described of preparing pure sodium β-naphthoxide. When heated with an excess of carbon dioxide at 110—120°, it is converted into β-sodoxynaphthoic acid,

$$ONa \cdot C_{10}H_6 \cdot CO_2H,$$

which differs from sodium β-hydroxynaphthoate, $OH \cdot C_{10}H_6 \cdot CO_2Na$, in that it is capable of absorbing nearly one equivalent of dry ammonia.

2-*Hydroxynaphthoic acid* [β-naphthol-1-carboxylic acid] melts when quickly heated at 156°, liberating gas, and decomposes into naphthol and carbon dioxide when boiled with water; the acid contains a small quantity of water as represented by the formula $4C_{11}H_8O_3,H_2O$.

T. M. L.

Isomerism and Tautomerism. Arthur Michael (*Ber.*, 1906, **39**, 203—211).—A discussion of the constitutions of ethyl formylphenylacetate, oxalacetic acid and its esters, and of dibenzoylacetylmethane. When carbon dioxide is passed into a solution of the sodium derivative of ethyl formylphenylacetate, an oil is precipitated which quickly changes to a solid melting at about 50°. Using sulphuric acid of sp. gr. of at least 1·36 as the precipitant, a solid is at once obtained which melts at 98—100°. The use of a weaker solution of sulphuric acid causes the separation of an oil which changes somewhat slowly to a solid which melts between 60° and 90° and appears to be a mixture of the forms melting respectively at 50° and 100°. The modification melting at 50° is more soluble and is more easily transformed into the liquid tautomeride than is the form which melts at 100°.

The use of phenylcarbimide (Wislicenus, Abstr., 1896, i, 552) to differentiate between the enolic and ketonic forms is inadmissible, since all the modifications of ethyl formylphenylacetate unite with this reagent to form the ethereal carbanilide which melts at 116°. Normal tertiary fatty amines, which unite only with enolic derivatives, are suitable reagents for the purpose in question, and, according to this criterion, all the forms of the ester are enolic.

[With Arthur Murphy, jun.]—When a 10 per cent. solution of sulphuric acid is slowly added at 0° to a solution of the sodium derivative of methyl oxalacetate (Wislicenus and Grossman, Abstr., 1894, i, 116), a modification of the ester is obtained which melts at 85—87° and is extraordinarily sensitive to heat, changing above 50°

into the ordinary form. Towards ferric chloride and other reagents, both modifications behave alike, and both are hydrolysed by hydrochloric acid into the oxalacetic acid which melts at 152°.

If to the mixture of the enolic and ketonic forms of dibenzoylacetylmethane, obtained by crystallising the ketonic form which melts at 107—110° from 50 per cent. alcohol, a trace of acetic acid is added, and Claisen's directions are then followed (*Annalen*, 1896, **291**, 78), a new modification of the ketonic tautomeride is obtained, which melts at 147—149°; the same substance can be prepared in a similar way from the ketonic form melting at 110° or from the enolic form by the action of acetyl chloride. From ethylene dibromide, both the new and the old ketonic modifications of dibenzoylacetylmethane crystallise unchanged below 25°; from methyl or ethyl alcohol, chloroform, or carbon tetrachloride, either form separates as a mixture of both modifications which melts at 126—136°, whilst the enolic tautomeride remains in solution. The new isomeride is at once enolised by benzene; so also is the old keto-derivative, contrary to Claisen's statement (*loc. cit.*). Of the two ketonic forms, the one with the higher melting point is the more stable and the less reactive. Tri*iso*butylamine, in a solution of benzene and ether, converts the less fusible form into an enol-keto-mixture; in the presence of light petroleum, the ketonic form melting at 110° is obtained. C. S.

Bromo- and Bromonitro-derivatives of *o*-Benzoylbenzoic Acid. Franz Kunckell and G. Knigge (*Ber.*, 1906, **39**, 194—196).—*Bromo-*o*-benzoylbenzoic acid*, $C_6H_4Br·CO·C_6H_4·CO_2H$, is obtained when *o*-benzoylbenzoic acid (Pechmann, Abstr., 1881, 96) is heated with water and bromine (2 mols.) for five hours at 120°. It crystallises from alcohol, melts at 156°, and dissolves readily in most organic solvents. When heated for 10—20 minutes with 5—10 times its weight of fuming nitric acid, it yields *bromotetranitro-*o*-benzoylbenzoic acid*, $C_{14}H_5O_{11}N_4Br$, which crystallises from alcohol in pale yellow plates melting at 178°. When *o*-benzoylbenzoic acid is heated with water and bromine (3 mols.) at 180°, a mixture of mono- and dibromobenzoylbenzoic acids and tetrabromobenzoic acid is obtained.

The *dibromo-*o*-benzoylbenzoic acid*, $C_{14}H_8O_3Br_2$, crystallises from benzene in colourless needles, melts at 194°, and is readily soluble in acetic acid, ether, or alcohol. The *tetrabromobenzoic acid* is sparingly soluble in alcohol, crystallises in yellow plates, and melts at 295°.

J. J. S.

Formation of Indigotin from Quinoline. Herman Decker and C. Kopp (*Ber.*, 1906, **39**, 72).—If the additive product of quinoline with ethyl chloroacetate is oxidised with potassium permanganate, the filtrate rendered alkaline, evaporated, and heated at 200°, it is converted into indigotin. Formylphenylglycine-*o*-carboxylic acid, $CO_2H·C_6H_4·N(CHO)·CH_2·CO_2H$, is probably an intermediate product of the oxidation. T. M. L.

Influence of Alkyloxy-groups on the Reactivity of α-Bromine Atoms in Aromatic Compounds. Alfred Werner [with P. Schorndorff and Ch. Chorower] (*Ber.*, 1906, **39**, 27—36).—The presence of *o*- or *p*-alkyloxy-groups greatly facilitates the replacement of *a*-halogen atoms by alkyloxy- or phenoxy-groups, a reaction which has been frequently observed by Zincke in derivatives of *p*-hydroxybenzyl bromide, $OH\cdot C_6H_4\cdot CH_2Br \longrightarrow OH\cdot C_6H_4\cdot CH_2\cdot OR$, but not in benzyl bromide itself.

Thus, *o*-methylcoumaric dibromide, $OMe\cdot C_6H_4\cdot CHBr\cdot CHBr\cdot CO_2H$, when boiled with methyl alcohol, yields the *a-methoxy*-ester,

$$OMe\cdot C_6H_4\cdot CH(OMe)\cdot CHBr\cdot CO_2Me,$$

which separates from light petroleum in colourless crystals and melts at 64°; the *a-methoxy-acid*, $C_{11}H_{13}O_4Br$, separates from light petroleum in colourless crystals and melts at 118°; the *potassium* salt forms large, clear, square crystals with a blue fluorescence. The dibromide of cinnamic acid, $C_6H_5\cdot CHBr\cdot CHBr\cdot CO_2H$, does not behave in this way, but is merely esterified. The *a-ethoxy-acid*,

$$OMe\cdot C_6H_4\cdot CH(OEt)\cdot CHBr\cdot CO_2H,$$

separates from light petroleum in large, asymmetric crystals and melts at 103°. The *a*-iso*propyloxy-acid*, $OMe\cdot C_6H_4\cdot CH(OPr^\beta)\cdot CHBr\cdot CO_2H$, separates from light petroleum in colourless prisms and melts at 125°. The action of phenol on methylcoumaric acid dibromide is more complex than that of alcohols; methyl bromide is apparently formed and *a*-p-*hydroxyphenylcoumaran*,  $O<\substack{C_6H_4\\CH_2}>CH\cdot C_6H_4\cdot OH$, is the chief product; it crystallises from much hot water in minute, glistening flakes and melts at 150—154°. The *acetyl* derivative, $C_{16}H_{14}O_3$, crystallises from concentrated alcoholic solution in thin, glistening scales or broad needles, melts at 102°, and has a normal molecular weight when dissolved in acetic acid. The *methyl ether* crystallises from alcohol in thin scales and melts at 94—95°.

Anisylideneacetophenone dibromide, $OMe\cdot C_6H_4\cdot CHBr\cdot CHBr\cdot COPh$, is acted on in a similar manner by methyl alcohol, the *a*-bromine atom being replaced by methoxyl. The *a-methoxy-ketone*,

$$OMe\cdot C_6H_4\cdot CH(OMe)\cdot CHBr\cdot COPh,$$

separates from methyl alcohol in colourless needles and melts at 101°. The *ethoxy-ketone*, $OMe\cdot C_6H_4\cdot CH(OEt)\cdot CHBr\cdot COPh$, crystallises from alcohol in long, colourless needles and melts at 70°. The *hydroxy-ketone*, $OMe\cdot C_6H_4\cdot CH(OH)\cdot CHBr\cdot COPh$, prepared by boiling with aqueous acetone, crystallises from light petroleum in long, colourless needles and melts at 78°. T. M. L.

2-Amino*iso*phthalic Acid. EMILIO NOELTING and CH. GACHOT (*Ber.*, 1906, **39**, 73—76).—When boiled with nitric acid of sp. gr. 1·4, 2-nitro-*m*-xylene yields *v*-dinitro-*m*-xylene, a *substance*,

$$NO_2\cdot C_6H_3Me\cdot CH_2\cdot NO_2\ (?),$$

which changes readily into an aldehyde, and 2-*nitro*-m-*toluic acid*, $C_8H_7O_4N$, melting at 217·5—218°. When oxidised with potassium permanganate in alkaline solution, this yields 2-*nitro*iso*phthalic acid*, $C_8H_5O_6N$, which is formed directly from 2-nitro-*m*-xylene by oxidation with potassium permanganate in presence of magnesium sulphate. It crystallises in white needles, commences to become brown at 287°, and is not completely melted at 300°. The *barium* salt was analysed; the *dimethyl* ester, $C_{10}H_9O_6N$, crystallises in glistening, white scales, melts at 129—130°, and undergoes partial hydrolysis when recrystallised from boiling water. The *hydrochloride* of 2-amino*iso*phthalic acid, obtained by reduction of the nitro-acid with zinc and concentrated hydrochloric acid, crystallises in white needles and on exposure to the air readily loses hydrogen chloride, forming the free *amino-acid*, $C_8H_7O_4N$; this crystallises from alcohol in yellow leaflets, melts above 260°, and is easily soluble in alcohol or ether. The *copper* salt, $C_8H_5O_4NCu$, is obtained as a green precipitate, which, after drying at 119°, has the composition $2C_8H_5O_4NCu,CuO$.

2-*Acetylaminoisophthalic acid*, $NHAc\cdot C_6H_3(CO_2H)_2$, is prepared by oxidising aceto-*m*-2-xylidide with potassium permanganate in presence of magnesium sulphate; it crystallises in long, slender, white needles, and on prolonged boiling with concentrated hydrochloric acid yields the hydrochloride of 2-amino*iso*phthalic acid. When titrated with methyl-orange as indicator, the acid neutralises only 1 mol. of sodium hydroxide; the *copper* salt, $NHAc\cdot C_6H_3(CO_2)_2Cu$, was analysed.

When cooled and diazotised with sodium nitrite and hydrochloric acid or with nitrosyl sulphate and concentrated sulphuric acid and "coupled" with phenol in alkaline solution, 2-amino*iso*phthalic acid forms the *azo*-derivative, $C_6H_3(CO_2H)_2\cdot N_2\cdot C_6H_4\cdot OH$, which is obtained in glistening, yellow, anhydrous scales or in red, spear-like needles containing $2/3H_2O$, which is lost at 115°. When dissolved in boiling water and allowed to cool slowly, the yellow modification is converted into the red; if this is heated with concentrated hydrochloric acid, it yields a yellow *product* which is insoluble in most solvents and cannot be reconverted into the red azo-compound. With *p*-cresol, diazotised 2-amino*iso*phthalic acid forms an *azo*-derivative, $C_{15}H_{12}O_5N_2$, which is obtained in two anhydrous modifications, red and yellow respectively.

G. Y.

Preparation of Chloro- and Bromo-phthalimides.

BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 161340).—The action of alkali hypochlorites on an aqueous suspension of phthalimide is very slow, whilst if the alkali salts of phthalimide are employed, partial hydrolysis to phthalamates occurs. If the phthalimide is suspended in acetic acid and sodium hypochlorite or hypobromite is added, chloro- or bromo-phthalimide is precipitated in a pure form.

C. H. D.

Synthesis of α-Amino-acids by means of Bromo-fatty Acids.

EMIL FISCHER and WILHELM SCHMITZ (*Ber.*, 1906, **39**, 351—356. Compare Fischer, Abstr., 1904, i, 890).—*α-Bromoisobutylmalonic acid*, $C_7H_{11}O_4Br$, prepared by brominating *iso*butylmalonic acid (Guthzeit, Abstr., 1882, 39), crystallises from benzene, melts at 139—141° (corr.), is readily soluble in water, alcohol, or ether, and when heated at its melting point under 12 mm. pressure evolves carbon dioxide and forms α-bromo*iso*hexoic acid, $CHMe_2\cdot CH_2\cdot CHBr\cdot CO_2H$, which boils at 126—128·5° under 9 mm. pressure. With this is partially or wholly identical the bromo*iso*hexoic acid formed by the action of bromine and phosphorus on *iso*hexoic acid prepared from *iso*amyl cyanide.

Ethyl γ-phenylethylmalonate, $CH_2Ph\cdot CH_2\cdot CH(CO_2Et)_2$, formed by boiling ethyl sodiomalonate with ω-chloroethylbenzene in alcoholic solution in a reflux apparatus, boils at 185—187° under 24 mm. pressure, and on hydrolysis with concentrated potassium hydroxide yields *γ-phenylethylmalonic acid*, $CH_2Ph·CH_2·CH(CO_2H)_2$. This crystallises from toluene in glistening, colourless leaflets, melts and evolves carbon dioxide at 142—144° (corr.), and is readily soluble in hot water, alcohol, or ether.

α-Bromo-γ-phenylethylmalonic acid, $CH_2Ph·CH_2·CBr(CO_2H)_2$, formed by brominating γ-phenylethylmalonic acid, crystallises from benzene in small, nodular aggregates or from water in microscopic needles or thin prisms, and melts and decomposes at 116—118° (corr.). *α-Bromo-γ-phenylbutyric acid*, $CH_2Ph·CH_2·CHBr·CO_2H$, crystallises from water in thin leaflets or from benzene in small, rectangular, thin plates, melts at 188—190° (corr.), and may be distilled, if rapidly heated, under 10 mm. pressure. When treated with 25 per cent. aqueous ammonia at 100° for one and a half hours or at the laboratory temperature for some days, it forms *α-amino-γ-phenylbutyric acid*, $CH_2Ph·CH_2·CH(NH_2)·CO_2H$; this crystallises from boiling water in glistening needles or stellate aggregates of small plates containing H_2O, which is lost at 80° in a vacuum. When quickly heated, the dry amino-acid becomes yellow at 247° and melts and decomposes at about 252° (corr.); it has an unpleasant, bitter taste, and is moderately soluble in boiling alcohol. The *hydrochloride* crystallises from hot hydrochloric acid in glistening leaflets; the boiling aqueous solution of the base dissolves copper oxide, forming a blue solution, from which the *copper* salt crystallises on cooling in small, light blue needles or long, slender prisms. G. Y.

Butadiene Compounds. XIV. Nitrophenyldimethylfulgenic Acids and their Yellow Fulgides. HANS STOBBE (*Ber.*, 1906, 39, 292—298. Compare this vol., i, 91, 92, 101).—[With KARL LEUNER.] —*δ-o-Nitrophenyl-αα-dimethylfulgenic acid*,

$$CMe_2:C(CO_2H)·C(CO_2H):CH·C_6H_4·NO_2,$$

prepared from *o*-nitrobenzaldehyde and ethyl teraconate, crystallises from dilute alcohol or 80 per cent. acetic acid; it is white with a yellow lustre and gives a yellowish-white *barium* salt,

$$C_{14}H_{11}O_6NBa,H_2O.$$

The corresponding *fulgide*, $C_{14}H_{11}O_5N$, prepared by means of acetyl chloride, crystallises from benzene with $\frac{1}{2}C_6H_6$ in bright yellow, lustrous leaflets and melts and decomposes at 155°.

δ-m-Nitrophenyl-αα-dimethylfulgenic acid, prepared in similar manner from *m*-nitrobenzaldehyde, crystallises from ether, acetic acid, or dilute alcohol, and is bright yellow in colour with a green tinge; it melts at 228° and gives a white *barium* salt, $C_{14}H_{11}O_6NBa,H_2O$. The *fulgide*, $C_{14}H_{11}O_5N$, crystallises from benzene either with C_6H_6 in large, well-formed, intensely yellow prisms, or in smaller yellow prisms not containing the solvent; both forms melt at 120·5°.

δ-p-Nitrophenyl-αα-dimethylfulgenic acid, prepared by means of *p*-nitrobenzaldehyde, crystallises from ether or dilute alcohol, has a feebly yellow colour with a brown lustre, and melts and decomposes at 234°; the *barium* salt, $C_{14}H_{11}O_6NBa,H_2O$, has a greenish-yellow colour which becomes yellow at 180°. The *fulgide* separates from benzene in orange-red crystals with C_6H_6, which rapidly effloresce, giving a bright orange-coloured powder similar in shade to lead iodide; from chloroform, long, yellow needles are obtained. The fulgide melts at 175—177°.

A table is given showing the relationships of colour presented by *αα*-dimethylfulgenic acid, its *o*-, *m*-, and *p*-nitrophenyl derivatives and their fulgides, and analogous derivatives of *ααδ*-triphenylfulgenic acid. The relation between colour and constitution is discussed in these cases.

W. A. D.

Sulphonic Derivatives of Naphthalic Anhydride.

Guido Bargellini (*Atti R. Accad. Lincei*, 1905, [v], **14**, ii, 688—696. Compare Francesconi and Bargellini, Abstr., 1903, i, 34).—The blue fluorescence exhibited by a solution of naphthalic anhydride in concentrated or fuming sulphuric acid is not due to the formation of any compound in the solution. If the liquid is kept for several months, the fluorescence diminishes continuously and sulphonaphthalic acid is formed. This change proceeds more rapidly on heating, and at temperatures above 100° disulphonaphthalic acid is also formed. Neither of these compounds exhibits fluorescence.

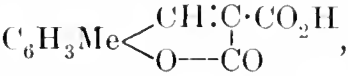
When fused with potassium hydroxide, sulphonaphthalic acid (Anselm and Zuckmayer, Abstr., 1900, i, 175) yields the hydroxynaphthalic anhydride melting at 287°. Since this anhydride has also been obtained from a 3-nitronaphthalic anhydride (Anselm and Zuckmayer, *loc. cit.*), and since also 4-hydroxynaphthalic anhydride melts at 257° (Graebe, Abstr., 1903, i, 408), sulphonaphthalic acid must have the sulphonic group in the 3-position, the two carboxyl groups being at positions 1 and 8.

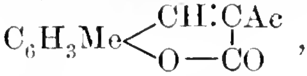
Disulphonaphthalic acid, $C_{10}H_4(CO_2H)_2(SO_3H)_2$ $[(CO_2H)_2:(SO_3H)_2 = 1:8:2:6]$, melts at about 220° and is readily soluble in water. The *barium* salt crystallises from water with $4H_2O$, and is precipitated, by addition of alcohol to its aqueous solution, as the dihydrate. The *anilide*, $C_{24}H_{14}O_6N_2S_2$, crystallises from alcohol in colourless plates decomposing at above 290° and is readily soluble in methyl alcohol and slightly so in ether, benzene, or carbon disulphide.

4 : 5-*Dibromo-3-sulphonaphthalic acid*, $C_{10}H_3Br_2(CO_2H)_2 \cdot SO_3H$, prepared by the action of bromine on a fuming sulphuric acid solution of naphthalic anhydride, crystallises from a mixture of ethyl acetate and ether in white needles melting at 204—205°, and dissolves in water, nitric acid, acetic acid, methyl, ethyl, or amyl alcohol, or dilute solutions of the alkali hydroxides or carbonates, and to a slight extent in benzene or carbon disulphide; it dissolves also in ammonia solution, giving a yellow liquid which deposits yellow, silky needles on cooling. Not one of these solutions, or that in concentrated sulphuric acid, is fluorescent. The *barium* salt, $C_{24}H_6O_{14}Br_4S_2Ba_3,8H_2O$, crystallises from water in white needles. The solution of the barium salt gives with copper acetate a greenish-blue, gelatinous precipitate, with lead acetate a white, flocculent precipitate, and with silver nitrate a white precipitate which blackens in the air.

T. H. P.

New Coumarins and some of their Derivatives. PH. CHUIT and FR. BOLSING (*Bull. Soc. chim.*, 1906, [iii], **35**, 76—90).—These coumarins and their derivatives were prepared by condensing hydroxyaldehydes with the appropriate ketonic acid or ester in presence of an amine, usually aniline or piperidine, a reaction first employed by Knoevenagel (Abstr., 1899, i, 116).

8-*Methylcoumarincarboxylicacid*,  $C_6H_3Me<\begin{array}{l}CH:C\cdot CO_2H\\ O—CO\end{array}$, prepared by condensing 3-methylsalicylaldehyde with malonic acid in presence of aniline hydrochloride, crystallises from benzene in colourless needles, melts at 142—143°, is readily soluble in hot benzene or acetic acid, soluble in alcohol (2·28 grams in 100 c.c. at 14°) and boiling water, slightly so in hot petroleum. The *ethyl* ester, obtained by using ethyl malonate in the condensation, forms colourless crystals, is inodorous, and melts at 81°. 8-*Methylcoumarin*, obtained by heating the acid, separates from alcohol in long, colourless needles, melts at 109—110°, boils at 178° under 20 mm. pressure, and has a feeble odour of coumarin. When ethyl acetoacetate is used in place of ethyl malonate in the condensation, 3-*acetyl*-8-*methylcoumarin*,


$$C_6H_3Me<\begin{array}{l}CH:CAc\\ O—CO\end{array},$$

is formed: this crystallises in brilliant, flattened, faintly yellow needles, is inodorous, and melts at 125·8—126·2°. The *phenylhydrazone* forms short, yellow tinted needles and melts at 168—169°; the *oxime*, yellowish-white needles melting and decomposing at 212—213°, and the *semicarbazone*, small, yellow crystals which melt and decompose at 224—225°.

When the Tiemann-Schotten reaction is applied to *m*-cresol, in addition to the *p*-aldehyde, 4-methylsalicylaldehyde (m. p. 59°) and 6-methylsalicylaldehyde (m. p. 31·5°) are produced. From the former, 7-*methylcoumarincarboxylic acid* was prepared: this crystallises in colourless leaflets, melts at 198·8—199·8°, is soluble in boiling acetic acid, slightly so in alcohol (0·45 gram in 100 c.c. at 14°) and in boiling water. The *ethyl* ester forms colourless, nacreous spangles from dilute alcohol, melts at 101·5—102·5°, and is readily soluble in warm alcohol, slightly so in light petroleum. 7-*Methylcoumarin*, obtained by heating the acid at 250—300°, crystallises from a mixture of alcohol and water in colourless leaflets, melts at 125·8—126·4°, boils at 171·5° under 11 mm. pressure, and possesses a strong odour of coumarin (compare Schmidt, *Inaug. Diss. Rostock*). 3-*Acetyl*-7-*methylcoumarin*, prepared by condensing the aldehyde with ethyl acetoacetate in presence of piperidine, crystallises from alcohol in brilliant, colourless needles, melts at 156—157°, and is inodorous; the *oxime* separates from alcohol in yellow needles and melts and decomposes at 224°.

5-*Methylcoumarincarboxylic acid*, similarly prepared from 6-methylsalicylaldehyde, crystallises from alcohol in colourless leaflets and melts at 162·5—163°; its solubility in alcohol is 1 gram in 100 c.c. at 14°. The *ethyl* ester crystallises from dilute alcohol in brilliant, colourless needles and melts at 122—122·5°. 5-*Methylcoumarin*, produced by heating the acid at 260°, crystallises from water in long needles, possesses a faint coumarin odour, and melts at 65—65·8°. 3-*Acetyl*-5-*methylcoumarin* forms yellow needles, melts at 115°, and is easily soluble in warm alcohol. The *oxime* crystallises in white needles and melts and decomposes at 214°.

6-*Methylcoumarincarboxylic acid*, prepared similarly from 5-methylsalicylaldehyde, crystallises from alcohol in yellowish-white needles, melts at 166·8°, and is soluble in acetic acid, less so in alcohol (1·22 grams in 100 c.c. at 14°). The *ethyl* ester separates from alcohol in large, colourless tables, is inodorous, melts at 103—104°, and is readily soluble in benzene, soluble in alcohol, and slightly so in water or light petroleum. 6-*Methylcoumarin* forms colourless needles from alcohol, melts at 74·6—75°, and boils at 303° under 725 mm. and at 174° under 14 mm. pressure. Its odour is slightly different from and more persistent than that of coumarin. 3-*Acetyl*-6-*methylcoumarin* separates on cooling a solution in warm alcohol in yellowish-white, nacreous leaflets and melts at 128—128·4°. The *phenylhydrazone* melts at 193—194°, the *oxime*, with decomposition, at 219°, and the *semicarbazone* at 211°, also with decomposition. T. A. H.

Action of Aqueous Solutions of Mercuric Acetate on Olefinic Compounds. Luigi Balbiano [with Vincenzo Paolini, A. Nardacci, U. Tonazzi, Enrico Luzzi, F. Bernardini, D. Cirelli, G. Mammola, and Gion Vespignani] (*Mem. R. Accad. Lincei*, 1905, [v], **5**, 515—578).—The greater part of this work has been already published (see Abstr., 1902, i, 808; ii, 109; 1904, i, 72 and 261), the new matter being as follows.

[With D. Cirelli.]—The action of mercuric acetate on asarone, which contains the propenyl group, should yield the glycol,

$$C_6H_2(OMe)_3{\cdot}CH(OH){\cdot}CHMe{\cdot}OH\ ;$$

if this compound is formed, it loses water, giving the *aldehyde*, $C_6H_2(OMe)_3{\cdot}CH_2{\cdot}CH_2{\cdot}CHO$, which boils at 184° under 14 mm. pressure and solidifies in lamellated aggregates melting at 47—48°. The *semicarbazone*, $C_{13}H_{19}O_4N_2$, crystallises from alcohol in shining plates melting at 157—158°.

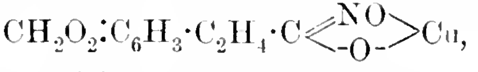
[With Vincenzo Paolini.]—On dehydrating the glycol,

$$OMe{\cdot}C_6H_4{\cdot}C_3H_5(OH)_2,$$

prepared by the action of mercuric acetate on anethole (Abstr., 1902, i, 808), by means of zinc chloride, it is converted into β-p-*methoxyphenylpropaldehyde*, $OMe{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}CHO$, which is a pale yellow liquid with a faint, aromatic odour, is soluble in alcohol or ether, and boils at 132—135° under 10 mm. pressure. The *semicarbazone*, $C_{11}H_{15}O_2N_3$, crystallises from alcohol in superposed laminæ, melts at 174°, and is soluble in all organic solvents. The *semicarbazone* of the isomeric aldehyde obtained by Bougault by the action of iodine and yellow mercuric oxide on anethole (Abstr., 1902, i, 452) crystallises from alcohol in feathery aggregates of white, opaque needles melting at 134°, and is soluble in all the organic solvents. On treating β-*p*-methoxyphenylpropaldehyde in strongly alkaline alcoholic solution with benzenesulphohydroxamic acid (compare Rimini, Abstr., 1901, i, 450) and afterwards neutralising the cold solution with acetic acid and treating with copper acetate, the *compound*,  $\mathrm{OMe{\cdot}C_6H_4{\cdot}C_3H_4}\!<\!\substack{\mathrm{NO}\\ \text{-O-}}\!>\!\mathrm{Cu}$, is obtained as a green powder slightly soluble in alcohol. On oxidation with moist silver oxide in presence of sodium hydroxide, β-*p*-methoxyphenylpropaldehyde yields a large proportion of resinous matter and a small quantity of anisic acid, whilst p-methoxyhydratropaldehyde (Bougault, *loc. cit.*) gives an almost quantitative yield of *p*-methoxyhydratropic acid.

When the glycol, $\mathrm{CH_2O_2{:}C_6H_3{\cdot}CH(OH){\cdot}CHMe{\cdot}OH}$, obtained by the action of mercuric acetate on *iso*safrole (Abstr., 1902, i, 808) is dehydrated by means of zinc chloride, it yields the *aldehyde*,

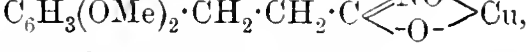
$$\mathrm{CH_2O_2{:}C_6H_3{\cdot}CH_2{\cdot}CH_2{\cdot}CHO},$$

which is a pale yellow liquid with a penetrating aromatic odour and boils at 145—150° under 22 mm. pressure. The *oxime*, $\mathrm{C_{10}H_{11}O_3N}$, crystallises from aqueous alcohol in faintly yellow, prismatic needles melting at 89°. The *semicarbazone*, $\mathrm{C_{11}H_{11}O_3N_3}$, crystallises from aqueous alcohol in white laminæ melting at 158°. On treatment with benzenesulphohydroxamic acid and subsequent neutralisation with acetic acid, it gives on addition of copper acetate (*vide supra*) the *compound*  $\mathrm{CH_2O_2{:}C_6H_3{\cdot}C_2H_4{\cdot}C}\!<\!\substack{\mathrm{NO}\\ \text{-O-}}\!>\!\mathrm{Cu}$, in the form of a bluish-green powder. When oxidised with silver oxide in presence of sodium hydroxide solution, the aldehyde is mainly resinified, but yields a small quantity of piperonylic acid; the isomeric 3 : 4-methylenedioxyhydratropaldehyde (Bougault, Abstr., 1901, i, 721) yields 3 : 4-methylenedioxyhydratropic acid.

On dehydrating the glycol, $\mathrm{C_6H_3(OMe)_2{\cdot}C_3H_5(OH)_2}$, obtained by the action of mercuric acetate on methyl *iso*eugenole (Abstr., 1904, i, 72), by means of zinc chloride, it is converted into the *aldehyde*,

$$\mathrm{C_6H_3(OMe)_2{\cdot}CH_2{\cdot}CH_2{\cdot}CHO},$$

which is a pale yellow, oily liquid with a faint, aromatic odour, is soluble in alcohol or ether, and boils at 146—147° under 6 mm. pressure. The *semicarbazone*, $\mathrm{C_{12}H_{17}O_3N_3}$, crystallises from alcohol in silky, white needles melting at 176—177°; the *oxime*, $\mathrm{C_{11}H_{15}O_3N}$, crystallises from alcohol in radiating laminæ melting at 62·5—63° and is soluble in ether. The *copper* compound,



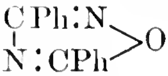
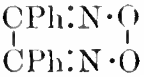
$$\mathrm{C_6H_3(OMe)_2{\cdot}CH_2{\cdot}CH_2{\cdot}C}\!<\!\substack{\mathrm{NO}\\ \text{-O-}}\!>\!\mathrm{Cu},$$

has been prepared. On oxidation with silver oxide in presence of sodium hydroxide, the aldehyde mostly resinifies but gives a small quantity of veratric acid, whilst the isomeric aldehyde,

$$\mathrm{C_6H_3(OMe)_2{\cdot}CHMe{\cdot}CHO}$$

(Bougault, Abstr., 1902, i, 452), yields 3 : 4-dimethoxyhydratropic acid.

T. H. P.

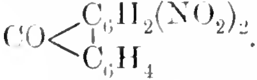
Oxidation of Aromatic Aldoximes with Amyl Nitrite. GAETANO MINUNNI and ROBERTO CIUSA (*Atti R. Accad. Lincei*, 1905, [v], **14**, ii, 518—525).—Oxidation of benzaldoxime by means of amyl nitrite in ethereal solution yields: (1) azobenzenyl peroxide (benzaldoxime peroxide), $\mathrm{CHPh{:}N{\cdot}O{\cdot}O{\cdot}N{:}CHPh}$, which was obtained by Beckmann by oxidising benzaldoxime with potassium ferricyanide (Abstr., 1889, 980), and melts and decomposes at 96°, not at 105°, as Beckmann stated: (2) dibenzenylazoxime,  $\begin{matrix}CPh{:}N\\ N{:}CPh\end{matrix}\!\!>\!O$, which has the melting point 102·5—104°, and not 108°, as stated in the literature; (3) benzildioxime peroxide,  $\begin{matrix}CPh{:}N{\cdot}O\\ CPh{:}N{\cdot}O\end{matrix}$; (4) a small quantity of a *compound* crystallising from alcohol in colourless needles melting at 152—153°.

m-Nitrobenzaldoxime, on oxidation in ethereal solution with amyl nitrite, yields: (1) m-*nitrobenzaldoxime peroxide*,

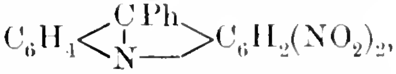
$$NO_2{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}O{\cdot}O{\cdot}N{:}CH{\cdot}C_6H_4{\cdot}NO_2,$$

which crystallises from a mixture of chloroform and alcohol in shining plates melting and decomposing at 105°; (2) di-*m*-nitrobenzenylazoxime, which was described by Stieglitz (Abstr., 1890, 254) and melts at 168°, the melting point 138°, given by Krümmel (Abstr., 1895, i, 661), being erroneous; the compound described by Bamberger and Scheutz (Abstr., 1901, i, 548) as di-*m*-nitrobenzenylazoxime has some other structure. T. H. P.

Chlorodinitrobenzophenone and its Conversion into Dinitrophenylacridine Derivatives. FRITZ ULLMANN and J. BROIDO (*Ber.*, 1906, **39**, 356—370. Compare Ullmann and Ernst, this vol., i, 205).—2-*Chloro*-3 : 5-*dinitrobenzophenone*, $C_{13}H_7O_5N_2Cl$, formed by the action of 2-chloro-3 : 5-dinitrobenzoyl chloride on benzene in presence of aluminium chloride, crystallises from glacial acetic acid in long, slightly yellow needles and melts at 149°. On treatment with sodium hydroxide in boiling alcoholic solution, it yields the *sodium* derivative of 3 : 5-dinitro-2-hydroxybenzophenone, which crystallises in orange-yellow needles, decomposes at about 318°, and has a bitter taste; the hydroxy-compound, $C_{13}H_8O_6N_2$, crystallises in small, yellow needles, melts at 116°, is soluble in benzene, ether, glacial acetic acid, or boiling alcohol, and gives a light yellow coloration with concentrated sulphuric acid and an intense yellow with dilute sodium hydroxide. 3 : 5-*Dinitro*-2-*methoxybenzophenone*, $OMe{\cdot}C_6H_2(NO_2)_2{\cdot}COPh$, formed in a poor yield by the action of sodium methoxide on the chloro-compound, crystallises in a colourless mass and melts at 83°.

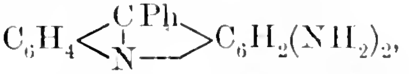
The action of anhydrous ammonia on 2-chloro-3 : 5-dinitrobenzophenone in boiling amyl-alcoholic solution leads to the formation of 3 : 5-*dinitro*-2-*aminobenzophenone*, $NH_2{\cdot}C_6H_2(NO_2)_2{\cdot}COPh$, which crystallises in yellowish-brown needles, melts at 166°, and when treated with sodium nitrite in concentrated sulphuric acid solution at the ordinary temperature and finally at 80—85° yields 2 : 4-*dinitrofluorenone*,  $CO\!<\!\begin{matrix}C_6H_2(NO_2)_2\\ C_6H_4\end{matrix}$. This crystallises from boiling glacial acetic acid in stellate aggregates of yellow needles, melts at 197°, and dissolves readily in benzene or chloroform, forming a yellow solution. 3 : 5-*Dinitro*-2-*ethylaminobenzophenone*, $C_{15}H_{13}O_5N_3$, formed by the action of ethylamine on 2-chloro-3 : 5-dinitrobenzophenone in alcoholic solution, crystallises in glistening, lemon-yellow leaflets, melts at 104°, and is readily soluble in benzene, chloroform, or hot alcohol, ether, or glacial acetic acid. When heated with copper powder and nitrobenzene at 200°, 2-chloro-3 : 5-dinitrobenzene forms 1 : 1′-*dibenzoyl-3 : 3′ : 5 : 5′-tetranitrodiphenyl*, $COPh{\cdot}C_6H_2(NO_2)_2{\cdot}C_6H_2(NO_2)_2{\cdot}COPh$, which melts at 186°.

3 : 5-*Dinitro-2-anilinobenzophenone*, $NHPh{\cdot}C_6H_2(NO_2)_2{\cdot}COPh$, is formed by fusing 2-chloro-3 : 5-dinitrobenzophenone with aniline and dissolving the product in alcohol ; it crystallises in small, glistening, orange-red needles, melts at 206°, and on prolonged heating with aniline yields 1 : 3-*dinitro-5-phenylacridine*,



$C_6H_4\left<\begin{matrix}CPh\\ |\\ N\end{matrix}\right>C_6H_2(NO_2)_2$,

which crystallises in lemon-yellow needles, melts at 240°, and dissolves in concentrated sulphuric or hydrochloric acid to form a yellow solution, from which the base separates in a yellow, flocculent precipitate on dilution. When reduced with stannous chloride and hydrochloric acid, it forms 1 : 3-*diamino-5-phenylacridine*,



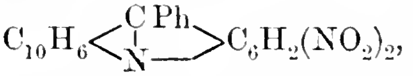
$$C_6H_4\left<\begin{matrix}CPh\\ |\\ N\end{matrix}\right>C_6H_2(NH_2)_2,$$

which is isolated as the *nitrate*, $C_{19}H_{15}N_3,HNO_3$; this crystallises from dilute acetic acid and dissolves in boiling alcohol to form a yellowish-brown solution having a slight green fluorescence. The *base* forms orange-yellow to brown crystals, melts at 159°, and dissolves in alcohol, forming an orange-yellow solution with slight green fluorescence, or in concentrated sulphuric acid, forming a yellow solution with brilliant green fluorescence ; the orange solution in concentrated hydrochloric acid becomes red when diluted with water. 1 : 3-*Diacetylamino-5-phenylacridine* crystallises in yellowish-brown needles, melts at 232—233°, and dissolves in concentrated sulphuric acid to form a yellow solution with green fluorescence.

3 : 5-*Dinitro-2-α-naphthylaminobenzophenone*,

$$COPh{\cdot}C_6H_2(NO_2)_2{\cdot}NH{\cdot}C_{10}H_7,$$

crystallises from glacial acetic acid in glistening, orange-red needles, melts at 190°, and when heated with concentrated sulphuric acid at 90—100° forms 9 : 11-*dinitro-7-phenyl-2 : 1-phenonaphthacridine*,



$C_{10}H_6\left<\begin{matrix}CPh\\ |\\ N\end{matrix}\right>C_6H_2(NO_2)_2$, which separates in yellow crystals, melts at 315°, is soluble in hot benzene or chloroform, and dissolves in concentrated sulphuric acid to form an orange-red solution; this on dilution deposits the base as a yellow, flocculent precipitate.

3 : 5-*Dinitro-2-β-naphthylaminobenzophenone*, $C_{23}H_{15}O_5N_3$, crystallises in orange-red needles, melts at 208°, and is moderately soluble in chloroform or glacial acetic acid, forming yellow solutions. 9 : 11-*Dinitro-7-phenyl-1 : 2-phenonaphthacridine*, $C_{23}H_{13}O_4N_3$, forms yellow crystals and melts at 320°.

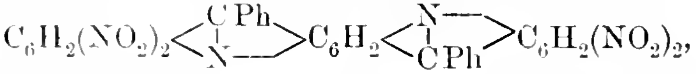
3 : 5-*Dinitro-2-*p-*aminoanilinobenzophenone*,

$$NH_2{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_2(NO_2)_2{\cdot}COPh,$$

formed by the action of an excess of *p*-phenylenediamine on 2-chloro-3 : 5-dinitrobenzophenone, crystallises from toluene in glistening, reddish-brown needles and melts at 221°. 1 : 3-*Dinitro-7-amino-5-phenylacridine*,

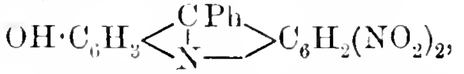
$NH_2{\cdot}C_6H_3\left<\begin{matrix}CPh\\ |\\ N\end{matrix}\right>C_6H_2(NO_2)_2$, crystallises from aniline in reddish-violet needles and melts above 360°.

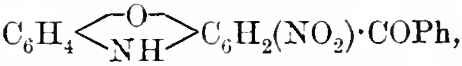
3′ : 5′ : 3″ : 5″-*Tetranitro*-1′ : 1″-*dibenzoyldiphenyl*-1 : 4-*phenylenediamine*, $C_6H_4[NH\cdot C_6H_2(NO_2)_2\cdot COPh]_2$, is formed together with 3 : 5-dinitro-2-*p*-aminoanilinobenzophenone by the interaction of 2-chloro-3 : 5-dinitrobenzophenone and *p*-phenylenediamine in molecular proportions; it crystallises in glistening, scarlet leaflets, melts at 318°, and dissolves in concentrated sulphuric acid, forming a reddish-brown solution. When heated at 100° with concentrated sulphuric acid and glacial acetic acid, it forms *tetranitrodiphenylquinacridine*,

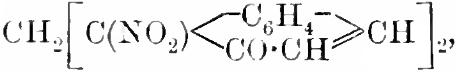


$$C_6H_2(NO_2)_2{<}\overset{CPh}{\underset{N}{|}}{>}C_6H_2{<}\overset{N}{\underset{CPh}{|}}{>}C_6H_2(NO_2)_2,$$

which is precipitated from its solution in boiling aniline by alcohol as a brown powder and dissolves sparingly in boiling toluene or glacial acetic acid.

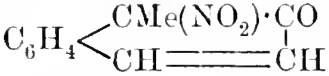
3 : 5-*Dinitro*-2-o-*hydroxyanilinobenzophenone*,
$OH\cdot C_6H_4\cdot NH\cdot C_6H_2(NO_2)_2\cdot COPh$,
crystallises in glistening, yellow leaflets, melts at 233°, and dissolves in aqueous sodium hydroxide, forming a reddish-brown, or in concentrated sulphuric acid forming a wine-red, solution. 1 : 3-*Dinitro*-9-*hydroxy*-5-*phenylacridine*,  $OH\cdot C_6H_3{<}\overset{CPh}{\underset{N}{|}}{>}C_6H_2(NO_2)_2$, forms a reddish-brown powder, melts at 233°, is readily soluble in chloroform, and dissolves in concentrated sulphuric acid, forming a red, or in aqueous sodium hydroxide forming a reddish-brown, solution.

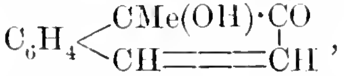
The action of aqueous sodium hydroxide on 3 : 5-dinitro-2-*o*-hydroxyanilinobenzophenone in boiling alcoholic solution leads to the formation of 3-*nitro*-5-*benzoylphenoxazine*,  $C_6H_4{<}\overset{O}{\underset{NH}{\;}}{>}C_6H_2(NO_2)\cdot COPh$, which crystallises from amyl alcohol or toluene in red needles, melts at 217°, and is readily soluble in boiling benzene or chloroform, but only sparingly so in boiling alcohol or ether. It dissolves in alcohol containing a few drops of concentrated aqueous sodium hydroxide to form a blue solution, from which it is precipitated unchanged on dilution with water; in concentrated sulphuric acid, it dissolves to form a red solution, which becomes blue when warmed. G. Y.

1-Methyl-β-naphthol and its Quinonoid Derivatives. K. FRIES and EDUARD HÜBNER (*Ber.*, 1906, **39**, 435—453. Compare Zincke, Abstr., 1903, i, 756).—Di-β-naphthylmethane is most readily prepared by the condensing action of sodium acetate on an alcoholic solution of β-naphthol and formaldehyde, and is converted by nitrous acid into the *diquinonitrole*,  $CH_2\left[C(NO_2){<}\overset{C_6H_4}{\underset{CO\cdot CH}{\;}}{>}CH\right]_2$, which crystallises in pale yellow plates melting and decomposing at 115°. It dissolves readily in acetone, chloroform, or ether, sparingly in benzene or alcohol, and is insoluble in alkalis. It is decomposed when boiled with a mixture of ether and glacial acetic acid, and when reduced with zinc and hydrochloric acid yields dinaphthylmethane. When warmed with an acetic acid solution of hydrogen chloride at 60°, the hydrocarbon yields a brown, crystalline compound, which is transformed into dinaphthaxanthen when dissolved in acetone and precipitated with water.

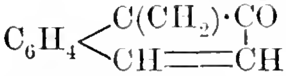
Dinaphthylmethane is readily decomposed by sodium hydroxide solution and zinc dust, yielding β-naphthol and 1-*methyl-β-naphthol*, $C_{10}H_6Me{\cdot}OH$; the amount of the methylnaphthol may be increased by adding formaldehyde and again heating with zinc dust and repeating the operations several times. It may be separated from dinaphthylmethane by means of its solubility in hot water. It crystallises in colourless needles, melts at 110°, dissolves readily in most organic solvents, and is volatile in steam. It does not couple with diazonium salts and is oxidised by nitric acid to phthalic acid. The *acetyl* derivative, $C_{13}H_{12}O_2$, crystallises from light petroleum in long, flat prisms melting at 66°. The *methyl ether* crystallises in colourless plates melting at 39°, and the *ethyl ether* also in plates melting at 50°. 6-*Bromo*-1-*methyl-β-naphthol*, $C_{10}H_5MeBr{\cdot}OH$, crystallises from benzene in colourless needles melting at 129°, and when oxidised yields 4-bromophthalic acid. The *ethyl ether*, $C_{10}H_5MeBr{\cdot}OEt$, melts at 66°, and the *acetyl* derivative, $C_{10}H_5MeBr{\cdot}OAc$, at 88°. 3 : 6-*Dibromo*-1-*methyl-β-naphthol*, $C_{10}H_4MeBr_2{\cdot}OH$, forms colourless needles, melts at 180°, and dissolves readily in cold ether, acetone, or chloroform; it also dissolves in aqueous sodium hydroxide, but is precipitated on the addition of much water. When oxidised, it yields 4-bromophthalic acid. The *acetyl* derivative, $C_{10}H_4MeBr_2{\cdot}OAc$, melts at 154°.

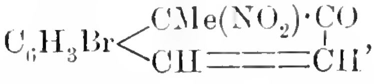
1-*Methyl-β-naphthylamine*, obtained by the action of calcium chloride ammonia on the naphthol at 270°, crystallises from light petroleum in colourless needles melting at 51°. It dissolves readily in most organic solvents, yields a sparingly soluble *sulphate* and an *acetyl* derivative, $C_{10}H_6Me{\cdot}NHAc$, melting at 189°.

Nitrous acid converts methyl-β-naphthol into 1 : 2-*methylnaphthaquinonitrole*,  $C_6H_4{<}\begin{matrix}CMe(NO_2){\cdot}CO\\ CH{=\!=\!=}CH\end{matrix}$, which crystallises from benzene in colourless, flat needles melting at 60°. When rapidly heated, it decomposes at 140°, evolving nitric oxide; it is readily soluble in the ordinary organic solvents, and when reduced yields methyl-β-naphthol. When its solution in a mixture of glacial acetic acid and ether is heated at 70° for some time, 1 : 2-*methylnaphtha-ψ-quinol*,

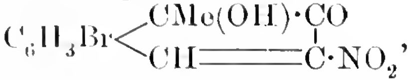


$$C_6H_4{<}\begin{matrix}CMe(OH){\cdot}CO\\ CH{=\!=\!=}CH\end{matrix},$$

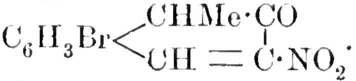
is obtained. It crystallises from water in glistening, colourless plates melting at 89°, and is readily soluble in most organic solvents. The *acetyl* derivative melts at 130°. 1 : 2-*Naphthamethylenequinone* (*β-naphthaquinone* 1-*methide*),  $C_6H_4{<}\begin{matrix}C(CH_2){\cdot}CO\\ CH{=\!=}CH\end{matrix}$, is obtained when sodium nitrite is added slowly to a glacial acetic acid solution of methylnaphthol, the mixture kept for eight hours, and then poured into cold water. It crystallises from light petroleum in compact, yellow needles, melts at 132°, and is insoluble in alkalis. When boiled for some time with alcohol, water, or acetone, it is converted into products which dissolve in alkalis.

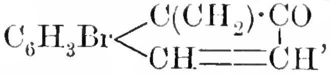
6-*Bromo*-1 : 2-*methylnaphthaquinonitrole*,  $C_6H_3Br{<}\begin{matrix}CMe(NO_2){\cdot}CO\\ CH{=\!=\!=}CH\end{matrix}$, crystallises in flat, compact needles, melts and decomposes at 99°, and when reduced yields bromomethylnaphthol. 6-*Bromo*-1 : 2-*methyl*-

naphtha-ψ-quinol, $C_{11}H_9O_2Br$, crystallises in yellow plates, melts at 84°, and is readily soluble in most organic solvents, but dissolves only slowly in alkalis. The *acetyl* derivative, $C_{13}H_{11}O_3Br$, melts at 101°. 6-*Bromo*-3-*nitro*-1 : 2-*methylnaphtha-ψ-quinol*,

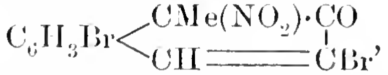


$$C_6H_3Br\Big<\begin{array}{l}CMe(OH)\cdot CO\\ CH=\!=\!=\!=C\cdot NO_2\end{array},$$

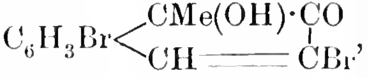
obtained by the action of nitric acid on the bromoquinonitrole or on bromomethylnaphthol, crystallises in golden-yellow plates, melts at 155°, and is only moderately soluble in ether, alcohol, benzene, or acetic acid. It dissolves in alkali hydroxides at the ordinary temperature. When reduced with sulphurous acid in acetic acid solution, it yields 6-*bromo*-3-*nitro*-1-*methyl-β-naphthol*,  $C_6H_3Br\Big<\begin{array}{l}CMe\!:\!C\cdot OH\\ CH:CNO_2\end{array}$, which crystallises in orange-red needles melting at 163°. This dissolves in hot sodium carbonate solution, yielding a violet-black coloured liquid, from which the unaltered naphthol crystallises on cooling. The *sodium* salt forms long, blackish-violet needles, but is hydrolysed by water. The alkali salts of methylnaphthol and of its bromo-derivative, and also the alkali salts of bromoaminomethylnaphthol, are not hydrolysed in the same manner, and it is suggested that the nitro-compound may have the ketonic constitution  $C_6H_3Br\Big<\begin{array}{l}CHMe\cdot CO\\ CH=C\cdot NO_2\end{array}$. 6-*Bromo*-3-*amino*-1-*methyl*-*β-naphthol*, obtained by reducing the nitrobromoquinonitrole with zinc and hydrochloric acid, crystallises from benzene in slender, colourless needles melting at 163°. It dissolves readily in ether, acetone, or alkali hydroxides. The *monoacetyl* derivative, $C_{13}H_{12}O_2NBr$, crystallises in colourless needles melting at 183°, and the *diacetyl* derivative in needles melting at 240°. With nitrous acid, the aminophenol yields a yellow diazophenol anhydride.

6-*Bromo*-1 : 2-*naphthamethylenequinone* (6-*bromo-β-naphthaquinone*-1-*methide*),  $C_6H_3Br\Big<\begin{array}{l}C(CH_2)\cdot CO\\ CH=\!=\!=CH\end{array}$, crystallises from light petroleum in yellow plates melting at 144°. It forms an *additive* compound with acetyl chloride, $C_{13}H_{10}O_2ClBr$, which forms compact needles melting at 158°.

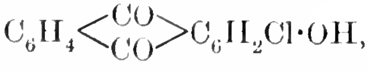
3 : 6-*Dibromo*-1 : 2-*methylnaphthaquinonitrole*,



$$C_6H_3Br\Big<\begin{array}{l}CMe(NO_2)\cdot CO\\ CH=\!=\!=\!=CBr\end{array},$$

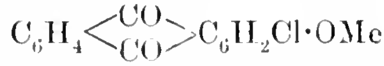
crystallises in colourless, flat needles melting at 130° and is the most stable of the *o*-quinonitroles. With acetic acid, it is slowly transformed into 3 : 6-*dibromo*-1 : 2-*methylnaphtha-ψ-quinol*,  $C_6H_3Br\Big<\begin{array}{l}CMe(OH)\cdot CO\\ CH=\!=\!=\!=CBr\end{array}$, which crystallises in colourless needles melting at 101°. The *acetyl* derivative melts at 152°.

J. J. S.

Constitution of Alizarin Monomethyl Ethers. HERMAN DECKER and ED. LAUBE (*Ber.*, 1906, **39**, 112—116, 526).—1-*Chloro*-2-*hydroxyanthraquinone*,  $C_6H_4\Big<\begin{array}{c}CO\\ CO\end{array}\Big>C_6H_2Cl\cdot OH$, is formed by boiling 2-hydroxyanthraquinone, which melts at 306° (corr.), with sodium hypochlorite in aqueous sodium hydroxide solution (Wedekind, D.R.-P.

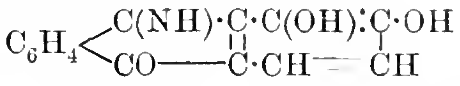
152172); it crystallises in small, yellow needles, or on slow evaporation of its solutions in rosettes of needles, melts at 226° (corr.), and dissolves in aqueous alkali hydroxides or carbonates to form red solutions; the *potassium* derivative is insoluble in cold water, but dissolves in alcohol, forming a violet solution. When fused with sodium ethoxide, it forms alizarin, and when heated with ammonia under pressure yields an *amino*-compound melting at 240—245° (corr.).

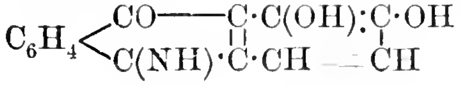
1-*Chloro-2-acetoxyanthraquinone*, $C_{14}H_6O_3ClAc$, formed by boiling the hydroxy-compound with acetic anhydride containing one to two drops of concentrated sulphuric acid, crystallises from alcohol in yellow, flocculent aggregates, melts at 163·5°, is hydrolysed only slowly by boiling aqueous alkali hydroxides, and dissolves in concentrated sulphuric acid, forming a red solution.

1-*Chloro-2-methoxyanthraquinone*,  $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_2Cl\cdot OMe$, is prepared by heating the sodium derivative of 1-chloro-2-hydroxyanthraquinone with methyl sulphate at 140°; after recrystallisation from alcohol or benzene, it melts at 223—224° (corr.). It is easily soluble in hot amyl alcohol or in concentrated sulphuric acid, forming an orange-red solution, and when heated with aqueous sodium hydroxide under pressure yields chiefly alizarin. When heated with sodium methoxide in methyl-alcoholic solution in a sealed tube at 100° for twelve hours, it yields alizarin monomethyl ether [1-hydroxy-2-methoxyanthraquinone], melting at 232—233° (Schunck and Marchlewski, Trans., 1894, **65**, 185).

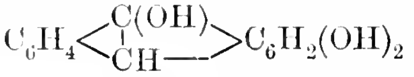
When heated with sodium ethoxide and ethyl alcohol, 1-chloro-2-methoxyanthraquinone yields a mixture of 1-hydroxy-2-methoxy- and 1-ethoxy-2-methoxy-anthraquinone; these are separated by treatment with benzene and aqueous sodium hydroxide. The monomethyl ether, melting at 232—233°, is obtained on acidification of the alkaline solution, whilst 1-ethoxy-2-methoxyanthraquinone crystallises from the benzene solution and melts at 169—170°. G. Y.

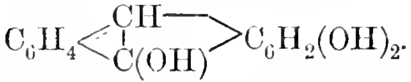
Reduction Products of Hydroxyanthraquinones. MAURICE PRUD'HOMME (*Bull. Soc. chim.*, 1906, [iii], **35**, 71—76).—When freshly precipitated alizarin, anthrapurpurin, or flavopurpurin is suspended in dilute acid and zinc dust is added, a brown or olive-green reduction product is formed, depending on the conditions of the experiment. Each of these reduction products is convertible into the same yellow substance by the action of acids. All three substances dissolve in alkalis to form solutions which are redder, but less intense, than that given by alizarin; they dye with the usual mordants in neutral solution, giving tints similar to those produced by alizarin, but in presence of acetic acid, owing apparently to the reduction of the mordant by the dyes, they give feeble tints or none at all with chromium and iron mordants.

Alizarinimide,  $C_6H_4<\begin{matrix}C(NH)\cdot C\cdot C(OH){:}C\cdot OH\\CO\text{——}C\cdot CH=CH\end{matrix}$ or

 $C_6H_4<\begin{matrix}CO\text{——}C\cdot C(OH){:}C\cdot OH\\C(NH)\cdot C\cdot CH=CH\end{matrix}$,

is prepared by heating alizarin with ammonia solution under pressure (Farbenfabriken vorm. Fr. Bayer & Co.). It crystallises from pyridine and when warmed with alkalis or acids is resolved into its generators. With aniline or phenylhydrazine, the imino-group is replaced by $:NPh$ or $:N\cdot NHPh$.

Alizarinimide is also produced when the precipitate, obtained by acidifying the brown solution, produced by the reduction of alizarin with hot ammonia solution and zinc dust, is washed, redissolved in ammonia, and oxidised by exposure to air. If, however, the brown solution itself is exposed to air, it also re-oxidises, forming the isomeride of alizarinimide represented by the alternative formula. It is considered, therefore, that the brown solution contains one form of the anthranol corresponding with alizarin, and the precipitate obtained by acidifying the brown solution consists of the other form, the possible formulæ being  $C_6H_4{<}\begin{matrix}C(OH)\\ |\\ CH\end{matrix}{>}C_6H_2(OH)_2$ and



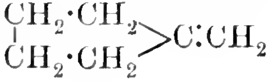
$$C_6H_4{<}\begin{matrix}CH\\ |\\ C(OH)\end{matrix}{>}C_6H_2(OH)_2.$$

The isomeride of alizarinimide is also formed when the brown, olive-green, or yellow reduction products of alizarin, referred to in the first paragraph, are dissolved in ammonia solution and exposed to air.

Two anthrapurpurinimides were obtained from anthrapurpurin: these resembled the alizarinimides. Flavopurpurin also yields a similar substance when its corresponding anthranol is treated with ammonia solution. T. A. H.

Preparation of Camphor from Borneol or *iso*Borneol. CHEMISCHE FABRIK AUF AKTIEN VORM. E. SCHERING (D.R.-P. 161306. Compare Abstr., 1905, i, 709; this vol., i, 28).—When borneol or *iso*borneol is dissolved in 95 per cent. acetic acid or light petroleum, water added, and a current of ozone passed through the solution at the ordinary temperature, camphor is formed readily. Camphene under similar conditions yields only camphenilone and formaldehyde. C. H. D.

Terpenes and Ethereal Oils. LXXIII. OTTO WALLACH (*Annalen*, 1905, **343**, 28—40. Compare Abstr., 1903, i, 103, 105, 567; 1904, i, 74, 104, 424, 752, 753, 754, 987, 1035; 1905, i, 147, 450, 709).—A special name is suggested for the methylene group, CH_2, which is found in semicyclic linking in many hydroaromatic and analogous compounds and in the methylenequinone and other substances studied by Auwers and Zincke. Such a methylene group has characteristic reactions which distinguish it from the same group in cyclic or acyclic molecules. Semmler has suggested the name "ψ-terpenes" for terpenes possessing this semicyclic methylene group. But such hydrocarbons do not bear to the terpenes the relation which ψ-compounds in general bear to their isomerides. It is consequently suggested that the acyclic methylene group found in limonene, carvone, citronellal, and *iso*pulegone should be called "methene." Thus, for example, the expression

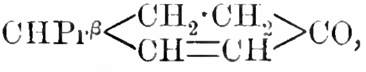


$$\begin{matrix}CH_2\cdot CH_2\\ |\\ CH_2\cdot CH_2\end{matrix}{>}C{:}CH_2$$

represents methene*cyclo*pentane (methene*cyclo*pentamethylene), the expression $\begin{array}{l}CH_2\cdot CH_2\cdot CH_2\\ |\\ CH_2\cdot CH_2\cdot CH_2\end{array}\!\!>C{:}CH_2$, methene*cyclo*heptane; β-phellandrene, $CHPr^{\beta}\!<\!\begin{array}{l}CH_2\cdot CH_2\\ CH{=}CH\end{array}\!\!>C{:}CH_2$, is called Δ^2-1-methene-4-*iso*propyl*cyclo*hexene or 1-methene-4-*iso*propyltetrahydrobenzene.

Experiments have been made in order to determine whether the tetrahydrocuminaldehyde obtained by oxidation by β-phellandrene (Abstr., 1905, i, 709) is present in the source of the phellandrene (oil of *Phellandrium aquaticum*) or whether it is formed in the oxidation of the phellandrene in the process of preparation.

Phellandrene was shaken with an equal quantity of water in a large flask with oxygen at the ordinary temperature and exposed to sunlight. Oxygen is rapidly absorbed; when the absorption has ceased after three days, a heavy, viscous oil remains, which is distilled in steam; at first, unchanged phellandrene distils over, mixed with a small amount of a substance which yields a semicarbazone. The non-volatile product does not contain a glycol. The *semicarbazone*, $C_9H_{14}{:}N\cdot NH\cdot CO\cdot NH_2$, melts at 183—184° and is converted by oxalic or sulphuric acid into an unsaturated *ketone*, $C_9H_{14}O$, which boils at 103—106° under 15 mm. or at 220—224° under the ordinary pressure; it has a sp. gr. 0·9387 and n_D 1·4788 at 26°. The ketone combines easily with sodium hydrogen sulphite, but is unchanged when treated with sodium hypobromite, and yields with hydrogen sulphide in ammoniacal solution a sulphur *compound* which melts at 121—122°. When reduced with sodium in moist ether, an alcohol is formed in small quantity with an odour resembling that of terpineol; it is oxidised in acetic acid solution to a saturated *ketone*, $C_9H_{16}O$, the *semicarbazone* of which melts at 188°. The ketone is oxidised by chromic acid in sulphuric acid solution to β-*iso*propyladipic acid. Hence it follows that the product of oxidation of β-phellandrene with free oxygen has the constitution

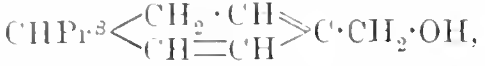


$$CHPr^{\beta}\!<\!\begin{array}{l}CH_2\cdot CH_2\\ CH{=}CH\end{array}\!\!>CO,$$

and is therefore 1-*iso*propyl-Δ^2-*cyclo*hexene-4-one. Further, the tetrahydrocuminaldehyde is an original constituent of the ethereal oils in which it is found, and not formed from the phellandrene. The conclusion may also be drawn from the experiments that the oxidation of an unsaturated compound by permanganate follows a different course from the oxidation of that compound by oxygen in the presence of water. The oxidation of the ethylene linking by oxygen is brought about by the addition of oxygen and the conversion of the double into the single linking, whilst the oxidation by permanganate brings about the addition of two hydroxyl groups at the ethylene linking. The reaction with oxygen is identical with that with ozone.

Attention is called to the fact that the odour of cyclic ketones depends on the relative positions of the carbonyl and the *iso*propyl group; thus, when they occupy *o*-positions relative to one another, the ketone has the odour of menthone, in the *m*-position relative to one another the odour of carvone, and in the *p*-position a cumin-like odour.

When β-phellandrene glycol, $CHPr^{\beta}\!<\!\begin{array}{l}CH_2\cdot CH_2\\ CH{=}CH\end{array}\!\!>C(OH)\cdot CH_2\cdot OH$, is oxidised by chromic acid in sulphuric acid solution. 1-*iso*propylhexene-4-one is formed. The glycol is converted into dihydrocuminalcohol,



$$CHPr^{\beta}<\begin{matrix}CH_2\cdot CH\\CH{=}CH\end{matrix}>C\cdot CH_2\cdot OH,$$

together with tetrahydrocuminaldehyde, on boiling with dilute sulphuric acid When the aldoxime (m. p. 87°) of the tetrahydrocuminaldehyde just mentioned is reduced in alcoholic solution with sodium, a base is obtained the carbamide of which melts at 160—161° and is identical with the base formed together with the carbamide of cuminylamine from nitro-β-phellandrene: the base, therefore, is probably a derivative of tetrahydrocuminylamine. These facts are in favour of the constitution of nitro-β-phellandrene previously suggested (Abstr., 1905, i, 709).

By the reactions above described, the question as to the occurrence of β-phellandrene together with the α-isomeride in the ethereal oil from *Eucalyptus amygdalina* has been decided; but a very small quantity of β-phellandrene is present. K. J. P. O.

Tertiary Alcohols of the *cyclo*Citrylidene Series. ALBERT VERLEY (D.R.-P. 160834. Compare Abstr., 1904, i, 880).—Certain cyclic citral derivatives combine with magnesium alkyl iodides, and the resulting compounds are decomposed by water to form tertiary alcohols. Thus, methyl *cyclo*citrylideneacetate combines with magnesium methyl iodide in ethereal solution to form the *compound*

$$\begin{matrix}CH_2\cdot CMe_2\cdot C\cdot CH{:}CH\cdot CMe_2\cdot O\cdot MgI\\ | \qquad\qquad\quad \| \\ CH_2{-}CH_2{-}CMe\end{matrix},$$

which is converted by water into cyclo*citrylidene*-tert.-*butyl alcohol*, $C_{14}H_{24}O$, which boils at 131° under 16 mm. pressure, has a sp. gr. 0·9003 at 15°, and has a fresh odour of violets. The same alcohol is obtained from ionone and magnesium methyl iodide. The corresponding *alcohol*, $C_{16}H_{28}O$, from ethyl *cyclo*citrylideneacetate and magnesium ethyl iodide, boils at 162° under 16 mm. pressure and has a sp. gr. 0·94229 at 15°. The *alcohol*, $C_{15}H_{26}O$, from ionone and magnesium ethyl iodide, boils at 153° under 15 mm. pressure.

The same series of tertiary alcohols may be obtained by combining the open chain esters of citrylideneacetic acid with magnesium alkyl iodides and converting the products into their cyclic isomerides by means of dilute acids. Thus, methyl citrylideneacetate and magnesium methyl iodide yield the *alcohol*,

$$CMe_2{:}CH\cdot CH_2\cdot CH_2\cdot CMe{:}CH\cdot CH{:}CH\cdot CMe_2\cdot OH,$$

which boils at 154° under 18 mm. pressure and has a sp. gr. 0·890 at 15°. C. H. D.

Action of Atmospheric Oxygen on Para Caoutchouc. EDGAR HERBST (*Ber.*, 1906, 39, 523—525).—When a current of purified air is passed for 140 hours through a hot solution of Para caoutchouc in benzene, two substances are obtained: a transparent, reddish-brown syrup, soluble in light petroleum, having the composition $C_{10}H_{16}O$, and an amorphous, friable, yellow solid of the composition $C_{10}H_{16}O_3$, insoluble in light petroleum. The latter is sparingly soluble in a mixture of benzene and light petroleum; from this solvent, a modification separates as a hard, glassy mass with substantially different physical properties. C. S.

Occurrence of β-Amyrin Acetate in some Varieties of Gutta-percha. PIETER VAN ROMBURGH and N. H. COHEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, **8**, 544—546. Compare Romburgh, Abstr., 1904, i, 905; this vol., i, 20).—The acetic ester obtained from the gutta-percha of *Payena Leerii* and from djelutung is identical with β-amyrin acetate (Vesterberg, Abstr., 1891, 165); it melts at 240—241° (corr.) and has $[\alpha]_D$ +81·1 in chloroform solution. The β-amyrin obtained on hydrolysis of the acetate crystallises in long, thin needles, melts at 197—197·5° (corr.), and has $[\alpha]_D$ +88° in chloroform or +98 in benzene solution: when treated with benzoic chloride in pyridine solution, it forms the benzoate, which crystallises in small, rectangular plates and melts at 234—235° (corr.).

The substance melting at 239—240°, obtained by Marek from the milky juice of *Asclepias syriaca* (Abstr., 1904, ii, 141), and α-balalban, obtained from balata by Tschirch and Schereschewski (Abstr., 1905, i, 713), also are identical with β-amyrin acetate. G. Y.

Heerabol Myrrh. ALEXANDER TSCHIRCH and W. BERGMANN (*Arch. Pharm.*, 1906, **243**, 641—654).—The material examined was a commercial sample of *Myrrha electa*: it consisted of reddish-brown pieces with a waxy fracture, and the following solvents dissolved the percentages of it indicated: alcohol, 36; ether, 29: chloroform, 31; light petroleum, 9; methyl alcohol, 38; water, 60; ethyl and methyl alcohols, 36; toluene, 30.

From an ethereal extract of the drug, ammonium carbonate and sodium carbonate alike dissolved nothing. One per cent. aqueous potassium hydroxide, however, dissolved the following two amorphous, greyish-yellow, neutral substances, which were separated in alcoholic solution by means of lead acetate, with which the first of them forms an insoluble precipitate, but not the second: *α-heerabo-myrrhol*, $C_{17}H_{24}O_5$, melting at 158—165°, and *β-heerabo-myrrhol*, $C_{15}H_{22}O_4$, melting at 116—124°.

From the residue insoluble in ether, alcohol extracted two brown, amorphous substances, soluble in dilute aqueous potassium hydroxide: *α-heerabo-myrrholol*, $C_{15}H_{22}O_7$ or $C_{30}H_{44}O_{14}$, melting at 207—220°, and *β-heerabo-myrrholol*, $C_{22}H_{36}O_{10}$, melting at 205—213°; of these, the first is precipitated from the solution by lead acetate, the second is not.

From the ethereal solution, after the extraction with alkali, the ether was driven off and the residue distilled with steam: an essential oil passed over. More of this oil was obtained by repeated distillation of the residue with very dilute aqueous potassium hydroxide: at the same time, a substance dissolved gradually in the alkali which melted at 188—197° and had the composition and reactions of α-heerabo-myrrhol. The *heeraboresen* finally remaining, $C_{26}H_{44}O_4$, melted at 98—104°. The *essential oil* was yellow, rather syrupy, and had the sp. gr. 1·046; it resinified readily.

The unusually high percentage of oxygen in these substances is noteworthy.

From the residue remaining after extraction with ether and alcohol, water extracted a mixture of a *gum* with an *enzyme* having the character of an oxydase. This mixture could not be separated into its constituents; it yielded 5·15 per cent. of ash containing calcium and magnesium, and gave pyrrole when heated with dry potassium hydroxide, furfuraldehyde when distilled with 12 per cent. hydrochloric acid, mucic acid when treated with nitric acid, and arabinose when hydrolysed with 5 per cent. sulphuric acid.

The *bitter principle* was not isolated in a state of purity.

The sample contained in 100 parts, approximately: heerabomyrrhol, a, 4 (and secondary 2), β, 2; heerabo-myrrholol, a, 3, β, 2; heeraboresen, 6; essential oil, 6—7 (and secondary 1·5); gum and enzyme, 61; impurities, 3—4; water, 5.

Two small specimens collected from unknown species of *Commiphora* in German East Africa were also examined cursorily. C. F. B.

d-Glucosephloroglucinol and β-Glucosan. EDUARD VONGERICHTEN and FR. MÜLLER (*Ber.*, 1906, **39**, 241—245).—When d-glucoseapigenin is boiled for five hours with a 25 per cent. solution of sodium hydroxide, it yields d-glucosephloroglucinol, which is in its turn partially converted into phloroglucinol and β-glucosan. From an aqueous solution containing d-glucosephloroglucinol and β-glucosan, the former is precipitated by the addition of lead acetate. d-*Glucosephloroglucinol* is a white, amorphous, hygroscopic powder dissolving readily in alcohol. In aqueous solution it has $[a]_D$ $-24·20°$ at 20°, in alcoholic solution, $[a]_D$ $-24·95°$ at 20°. It is unaffected by yeast or emulsin and reduces Fehling's solution only after having been boiled with mineral acids. It reacts with diazonium salts to form disazo-compounds: d-*glucosephloroglucinoldisazochlorobenzene*, $C_{24}H_{22}O_8N_4Cl_2$, is a reddish-brown, flocculent precipitate obtained from p-chlorophenyldiazonium chloride; d-*glucosephloroglucinoldisazobenzene*, $C_{24}H_{24}O_8N_4$, obtained from diazobenzene chloride, forms a reddish-brown, crystalline mass, soluble in alkalis.

β-Glucosan, obtained as described above, forms large, rhombic plates melting at 177—178° and is identical with Tanret's lævoglucosan (Abstr., 1894, i, 564).

The tribenzoyl derivative, in contradistinction to the triacetyl compound, is scarcely hydrolysed by hydrochloric acid. A boiling solution of baryta-water changes β-glucosan into a *hydrate*, which melts at 108° and in a vacuum loses water, re-forming β-glucosan. β-Glucosan is almost unaffected by bromine or potassium permanganate in neutral solution, but is converted into dextrose by hydrochloric acid. C. S.

Brazilin and Hæmatoxylin. JOSEF HERZIG and JACQUES POLLAK (*Ber.*, 1906, **39**, 265—267. Compare Abstr., 1903, i, 270, 713; 1904, i, 81; 1905, i, 605).—On warming on the water-bath a solution of tetramethylhæmatoxylone in glacial acetic acid with phenylhydrazine, a *compound*, $C_{22}H_{12}ON_2(OMe)_4$, is obtained, analogous with the substance prepared in a similar manner from trimethylbrazilone; it crystallises from ethyl acetate in yellow needles, melts at 234—237°, and is not affected by acetic anhydride or an excess of phenylhydrazine.

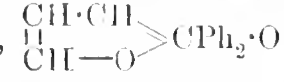
The phenylhydrazine derivative of trimethylbrazilone (*loc. cit.*) cannot be directly acetylated, but when heated with acetic anhydride, sodium acetate, and zinc dust, a reduced *monoacetyl* derivative,

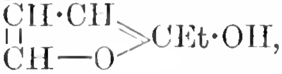
$$C_{22}H_{11}ON_2(OMe)_3\cdot OAc,$$

is obtained; this crystallises from alcohol, melts at 214—217°, and when hydrolysed gives a product which is oxidised by ferric chloride to the original phenylhydrazine derivative melting at 240—243°.

The bearing of these facts on the structure of brazilin is discussed.

W. A. D.

Grignard Syntheses in the Furan Group. WILLIAM J. HALE, W. D. MCNALLY, and C. J. PATER (*Amer. Chem. J.*, 1906, **35**, 68—78).—*Diphenyl-2-furylcarbinol*,  $\left.\begin{array}{l}CH\cdot CH\\ \|\\ CH-O\end{array}\right>CPh_2\cdot OH$, obtained by treating ethyl pyromucate with magnesium phenyl bromide and decomposing the product with water, crystallises in colourless, rhombic prisms, melts at 92·4° (corr.), is soluble in ether, alcohol, chloroform, benzene, ethyl acetate, or warm light petroleum, and gradually changes into a dark red, gummy mass; its *methyl ether* is a colourless oil which boils at 206—207° under 26 mm. pressure and has a sp. gr. 1·1195 at 20°.

2-*Furyldiethylcarbinol*,  $\left.\begin{array}{l}CH\cdot CH\\ \|\\ CH-O\end{array}\right>CEt\cdot OH$, was obtained as a pale yellow liquid which had a pleasant, ethereal odour and gradually changed into a dark brown, crystalline mass; it could not be purified by distillation, as it readily suffers decomposition with formation of *β-2-furyl-α-methyl-β-ethylethylene* [*γ-furyl-Δ^β-amylene*],

$$C_4H_3O\cdot CEt\colon CHMe,$$

which crystallises in colourless needles or prisms, melts at 249° (corr.), is soluble in chloroform, benzene, carbon disulphide, ether, or light petroleum, is insoluble in water, and decolorises a solution of bromine in carbon disulphide.

By the action of magnesium methyl iodide on ethyl pyromucate, an unstable, red liquid is produced.

Dibenzyl-2-furylcarbinol, $C_4OH_3\cdot C(C_7H_7)_2\cdot OH$, crystallises in silky needles, melts at 82·7° (corr.), is soluble in the usual organic solvents and insoluble in water, and is much more stable than the corresponding diphenyl derivative; its *methyl ether* crystallises in long, colourless needles and melts at 61·2° (corr.).

Furylene-2:5-bisdiphenylcarbinol, $C_4OH_2(CPh_2\cdot OH)_2$, obtained by the action of magnesium phenyl bromide on ethyl dehydromucate, forms small, colourless, rhombic crystals, melts at 165·5° (corr.), is soluble in alcohol, ether, acetone, benzene, or chloroform, and is more stable than diphenyl-2-furylcarbinol; its *methyl ether* crystallises in groups of white needles and melts at 88·2° (corr.); the *ethyl ether* forms rhombic prisms and melts at 171° (corr.).

Furylene-2:5-bisdibenzylcarbinol, $C_4OH_2[C(C_7H_7)_2\cdot OH]_2$, is a fairly stable substance of a light straw colour; it boils and partially decomposes at 193—195° under 30 mm. pressure, has an agreeable odour, a

sp. gr. 1·126 at 27°, and is soluble in all the usual solvents except light petroleum and water.
E. G.

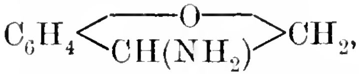
1- and 2-Aminocoumaran (Coumaranamine). Richard Stoermer and W. König (*Ber.*, 1906, **39**, 492—499. Compare Stoermer and Calov, Abstr., 1901, i, 336).—Hydrocoumarilic acid (coumaranilic acid), prepared by the reduction of coumarilic acid in alkaline solution by sodium amalgam, melts at 116·5°; its ethyl ester boils at 273° and melts at 23°. *Coumaranilic hydrazide*, prepared from ethyl coumaranilate and hydrazine hydrate, separates from alcohol in snow-white needles and melts at 148°. *Dicoumaranilic hydrazide*, $C_8H_7O\cdot CO\cdot NH\cdot NH\cdot CO\cdot C_8H_7O$, crystallises in needles. *Coumaranilic azoimide*, $N_3\cdot CO\cdot C_8H_7O$, prepared by dissolving coumaranilic hydrazide in water and gradually adding sodium nitrite (2 mols.) and dilute acetic acid, is a snow-white solid and melts at 32°. It is probably formed as an intermediate product in the preparation of dicoumaranilic hydrazide from coumaranilic hydrazide; thus

$$C_8H_7O\cdot CO\cdot NH\cdot NH_2 + N_3\cdot CO\cdot C_8H_7O = N_2H_2(CO\cdot C_8H_7O)_2 + HN_3$$

represents the formation of dicoumaranilic hydrazide. When coumaranilic azoimide is heated with absolute alcohol, 1-carboxyethylaminocoumaran (1-urethylcoumaran), $C_8H_7O\cdot NH\cdot CO_2Et$, melting at 105°, is formed. *Phenylurethylcoumaran*, prepared from coumaranilic azoimide and phenol, forms glistening leaflets and melts at 151°. *Dicoumaranyl carbamide*, $CO(NH\cdot C_8H_7O)_2$, prepared by boiling the azoimide with water, separates from dilute alcohol as a crystalline powder and melts at 205°. *Coumaranilic anilide*, prepared by the action of aniline on the azoimide, separates from dilute alcohol in glistening scales and melts at 104°.

Coumarone was formed as one of the products of the action of cold concentrated hydrochloric acid on coumaranylurethane.

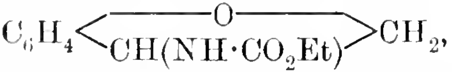
Coumaranone was prepared by the dehydration of phenoxyacetic acid with phosphoric oxide (compare Stoermer and Bartsch, Abstr., 1901, i, 94). Its oxime, when reduced by sodium amalgam and glacial acetic acid, yielded 2-*aminocoumaran*,



$$C_6H_4{<}\begin{matrix}O\\ CH(NH_2)\end{matrix}{>}CH_2,$$

as a yellow oil which boils at 122° under 18 mm. pressure. It has the sp. gr. 1·1303 at 17° and n_D 1·5645 at 19°. Its *hydrochloride* melts and decomposes at 226°; its *platinichloride* decomposes at 220°; its *aurichloride* melts and decomposes at 161°.

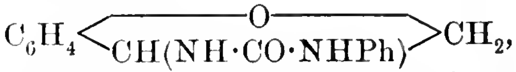
2-*Carboxyethylaminocoumaran* (2-*urethylcoumaran*),



$$C_6H_4{<}\begin{matrix}O\\ CH(NH\cdot CO_2Et)\end{matrix}{>}CH_2,$$

prepared from 2-aminocoumaran and ethyl chlorocarbonate, separates from dilute alcohol in needles and melts at 101·5°.

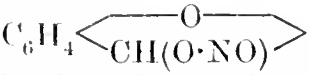
Coumaranylphenylcarbamide,



$$C_6H_4{<}\begin{matrix}O\\ CH(NH\cdot CO\cdot NHPh)\end{matrix}{>}CH_2,$$

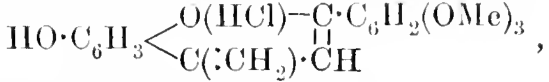
prepared from 2-aminocoumaran and phenylcarbimide, separates from dilute alcohol in needles and melts at 204°.

Coumarone and ammonium chloride are formed when 2-aminocoumaran hydrochloride is heated.

2-*Coumaranol nitrite*,  $C_6H_4\Big<\begin{array}{c}O\\ CH(O\cdot NO)\end{array}\Big>CH_2$, prepared from 2-aminocoumarone hydrochloride and potassium nitrite, separates from dilute alcohol in glistening leaflets and melts at 65°. When heated, it decomposes into coumarone and nitrous acid. A. McK.

7-Hydroxy-2-*o-m-p*-trimethoxyphenyl-4-methylene-1:4-benzopyran and its Derivatives. CARL BÜLOW and CARL SCHMID (*Ber.*, 1906, **39**, 214—225. Compare Abstr., 1901, i, 400, 559; 1904, i, 262; 1905, i, 150).—The *copper* derivative of 2:3:4-trimethoxybenzoylacetone (Blumberg and Kostanecki, Abstr., 1903, i, 644) separates from dilute alcohol in clusters of needles and melts at 150—152°.

Resorcinol condenses with 2:3:4-trimethoxybenzoylacetone in the presence of dry hydrogen chloride to form 7-*hydroxy*-2-o-m-p-*trimethoxyphenyl*-4-*methylene*-1:4-*benzopyran hydrochloride*,



$$HO\cdot C_6H_3\Big<\begin{array}{l}O(HCl)\text{—}C\cdot C_6H_2(OMe)_3\\ \quad\quad\quad\;\; \| \\ C(:CH_2)\cdot CH\end{array},$$

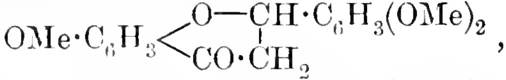
which is obtained in clusters of dark yellow needles soluble in water or alcohol. A concentrated aqueous solution is orange-yellow in colour, turning red on dilution owing to hydrolytic dissociation. The *sulphate* forms tufts of silky needles which melt at 203° to a steel-blue liquid. The *picrate*, $C_{25}H_{21}O_{12}N_3$, forms minute, yellow needles which darken at 100°, become black at 200°, and melt and decompose at 212°. The free *base*, obtained from an aqueous solution of the hydrochloride by adding a slight excess of ammonium hydroxide and then neutralising with acetic acid, separates in light red, microcrystalline flocks, sinters at 95°, becomes dark and melts at 105—110°. The *acetyl* derivative, $C_{21}H_{20}O_6$, melts at 245—247°.

By reduction with zinc dust and acetic acid in the presence of acetic anhydride, the base yields a *dihydro*-derivative, $C_{21}H_{22}O_6$, which forms a greenish-yellow, amorphous powder and melts at 230—235°.

By brominating the hydrochloride in acetic acid, a dibromo-derivative is obtained, the *hydrobromide* of which, $C_{19}H_{18}O_5Br_2,HBr$, forms red, prismatic crystals which blacken on heating, but do not melt below 270°. The *base*, $C_{19}H_{18}O_5Br_2$, forms small, greenish-brown needles which melt and decompose at 215°. Bromination of the hydrochloride in the presence of anhydrous sodium acetate leads to the formation of a *tetrabromo*-derivative, $C_{19}H_{18}O_5Br_4$, which crystallises in dark red prisms and does not melt below 300°.

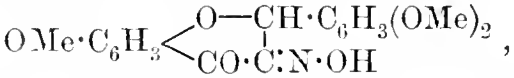
7-*Hydroxy*-2-o-m-p-*trihydroxyphenyl*-4-*methylene*-1:4-*benzopyran hydrochloride*, $C_{16}H_{12}O_5,HCl$, is obtained by heating the corresponding trimethoxy-compound at 150—180° with hydrochloric acid. It crystallises in small, red leaflets with blue reflex, and in solution is more stable than the hydrochloride of the trimethyl ether. The *base*, $C_{16}H_{12}O_5$, crystallises in minute, brown needles which partially decompose on exposure to air. Concentrated sulphuric acid dissolves it, forming an orange-red, non-fluorescent solution. C. S.

Synthesis of 6 : 2′ : 4′-Trihydroxyflavonol. E. BONIFAZI, STANISLAUS VON KOSTANECKI, and JOSEF TAMBOR (*Ber.*, 1906, **39**, 86—91).—2:4-Dimethoxybenzaldehyde and quinacetophenone monomethyl ether (Abstr., 1904, i, 440) condense in warm alcoholic sodium hydroxide solution, forming *2'-hydroxy-5' : 2 : 4-trimethoxychalkone*, $\mathrm{OH\cdot C_6H_3(OMe)\cdot CO\cdot CH{:}CH\cdot C_6H_3(OMe)_2}$, which crystallises in slender, orange needles, melts at 118°, and gives a red coloration with concentrated sulphuric acid. When heated with acetic anhydride and sodium acetate, it yields *2'-acetoxy-5' : 2 : 4-trimethoxychalkone*, $\mathrm{C_{15}H_8O_2(OMe)_3\cdot OAc}$, which crystallises in yellow needles and melts at 87°, and *6 : 2' : 4'-trimethoxyflavanone*,



$$\mathrm{OMe\cdot C_6H_3}<\begin{matrix}\mathrm{O—CH\cdot C_6H_3(OMe)_2}\\ \mathrm{CO\cdot CH_2}\end{matrix},$$

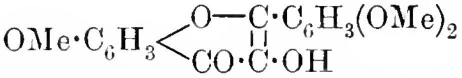
which is formed also by boiling 2'-hydroxy-5' : 2 : 4-trimethoxychalkone with alcoholic hydrochloric acid in a reflux apparatus. It crystallises in yellow prisms, melts at 160°, and gives a red coloration with concentrated sulphuric acid. The iso*nitroso*-derivative,



$$\mathrm{OMe\cdot C_6H_3}<\begin{matrix}\mathrm{O—CH\cdot C_6H_3(OMe)_2}\\ \mathrm{CO\cdot C{:}N\cdot OH}\end{matrix},$$

formed by the action of amyl nitrite and hydrochloric acid on the preceding compound in alcoholic solution, crystallises in small, yellow needles, melts and decomposes at 173—175°, dissolves in aqueous sodium hydroxide to form a yellow solution, and dyes with cobalt mordants orange, uranium, cadmium, and lead mordants yellow, and copper mordants brown.

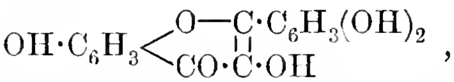
6 : 2' : 4'-Trimethoxyflavonol,



$$\mathrm{OMe\cdot C_6H_3}<\begin{matrix}\mathrm{O—C\cdot C_6H_3(OMe)_2}\\ \mathrm{CO\cdot C\cdot OH}\end{matrix},$$

prepared by boiling the *iso*nitroso-compound with sulphuric acid in glacial acetic acid solution, crystallises in yellow spears, melts at 193°, when warmed with dilute sodium hydroxide forms a sparingly soluble yellow *sodium* derivative, dyes with alumina mordants a light yellow, and dissolves in concentrated sulphuric acid to form a greenish-yellow solution which becomes almost colourless and shows a green fluorescence. The *acetyl* derivative crystallises from dilute alcohol in prismatic needles and melts at 162°.

6 : 2' : 4'-Trihydroxyflavonol,



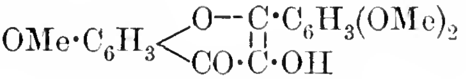
$$\mathrm{OH\cdot C_6H_3}<\begin{matrix}\mathrm{O—C\cdot C_6H_3(OH)_2}\\ \mathrm{CO\cdot C\cdot OH}\end{matrix},$$

formed by boiling the trimethoxy-compound with concentrated hydriodic acid, crystallises in light yellow needles containing $\mathrm{H_2O}$, which is lost at 130°, melts at 285°, and dissolves in dilute sodium hydroxide to form a greenish-yellow solution with strong green fluorescence, in concentrated sulphuric acid to form a yellow solution with slight green fluorescence. It dyes fibres mordanted with alumina yellow, with iron salts, olive-brown to almost black. When boiled with acetic anhydride and sodium acetate, it forms the *tetra-acetyl* derivative, $\mathrm{C_{15}H_6O_2(OAc)_4}$, which crystallises from dilute alcohol in white needles and melts at 163°. G. Y.

Dyeing Properties of 7 : 2' : 4'-Trihydroxyflavonol. Stanislaus von Kostanecki, Victor Lampe, and S. Triulzi (*Ber.*, 1906, **39**, 92—96).—*2'-Hydroxy-4' : 2 : 4-trimethoxychalkone*,

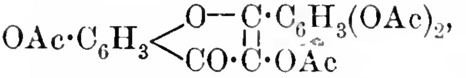
$$\mathrm{OH\cdot C_6H_3(OMe)\cdot CO\cdot CH{:}CH\cdot C_6H_3(OMe)_2},$$

is obtained in the form of its yellow *sodium* derivative by the condensation of 2 : 4-dimethoxybenzaldehyde with resacetophenone monomethyl ether (pæonol) in hot alcoholic sodium hydroxide solution; when liberated by means of hydrochloric acid and recrystallised from alcohol, the chalkone forms yellow needles, melts at 157°, and gives a red coloration with concentrated sulphuric acid. 2′-Acetoxy-4′ : 2 : 4-trimethoxychalkone, $C_{15}H_8O_2(OMe)_3\cdot OAc$, crystallises from dilute alcohol in yellow, nodular aggregates and melts at 110—112°. When boiled with alcoholic hydrochloric acid in a reflux apparatus for twenty-four hours, the chalkone is partially converted into 7 : 2′ : 4′-*trimethoxyflavanone*,  $\mathrm{OMe\cdot C_6H_3}<\begin{array}{l}\mathrm{O-\overset{}{C}H\cdot C_6H_3(OMe)_2}\\ \mathrm{CO\cdot \overset{|}{C}H_2}\end{array}$, which is extracted from the mixture by much boiling water; it crystallises from dilute alcohol in white needles, melts at 139°, and dissolves in alcoholic sodium hydroxide to a yellow, in concentrated sulphuric acid to a red, solution. The iso*nitroso*-derivative,  $\mathrm{OMe\cdot C_6H_3}<\begin{array}{l}\mathrm{O-CH\cdot C_6H_3(OMe)_2}\\ \mathrm{CO\cdot \overset{|}{C}{:}N\cdot OH}\end{array}$, forms small, yellow crystals, melts and decomposes at 172°, dissolves in dilute sodium hydroxide to form a yellow solution, and dyes with cobalt mordants yellow.

7 : 2′ : 4′-*Trimethoxyflavonol*,  $\mathrm{OMe\cdot C_6H_3}<\begin{array}{l}\mathrm{O-C\cdot C_6H_3(OMe)_2}\\ \mathrm{CO\cdot \overset{||}{C}\cdot OH}\end{array}$, crystallises from alcohol in yellow spears, melts at 205°, and dyes with aluminium mordants a light yellow; when warmed with aqueous sodium hydroxide, it forms a sparingly soluble, yellow *sodium* derivative, and dissolves in concentrated sulphuric acid to form a yellow solution with an intense bluish-green fluorescence. The *acetyl* derivative,

$$C_{15}H_{16}O_2(OMe)_3\cdot OAc,$$

crystallises from dilute alcohol in short prisms and melts at 189—191°.

7 : 2′ : 4′-*Trihydroxyflavonol* (*resomorin*), formed by boiling 7 : 2′ : 4′-trimethoxyflavonol with concentrated hydriodic acid, separates from dilute alcohol as a gelatinous mass; its behaviour towards metallic mordants is the same as that of 6 : 2′ : 4′-trihydroxyflavonol (see preceding abstract) and of morin. The character of the last-named substance as a dye must depend therefore on the presence of the group –CO·C(OH)–, and not on the presence of a hydroxyl in the *peri*-position to the carbonyl group. When boiled with acetic anhydride and sodium acetate, resomorin forms the *tetra-acetyl* derivative,  $\mathrm{OAc\cdot C_6H_3}<\begin{array}{l}\mathrm{O-C\cdot C_6H_3(OAc)_2}\\ \mathrm{CO\cdot \overset{||}{C}\cdot OAc}\end{array}$, which crystallises in rosettes of small, stout needles and melts at 129—130°. G. Y.

Cotarnine Ferrichloride. Arnold Voswinkel (D.R.-P. 161400).—On mixing solutions of ferric chloride and cotarnine hydrochloride in absolute alcohol, *cotarnine ferrichloride*, $C_{12}H_{13}O_3N,HFeCl_4$, is precipitated in orange leaflets, slowly agglomerating to form ruby-red crystals. The same compound is obtained on heating anhydrous ferric chloride with cotarnine hydrochloride in a vacuum. The salt dissolves in water or dilute alcohol and is decomposed on boiling. It finds therapeutic application as a styptic. C. H. D.

Transformation of α-Methylmorphimethine into the β-Compound by Heat. Crystallographic Behaviour of the Two Isomerides. ROBERT PSCHORR, HEINRICH ROTH, and F. TANNHÄUSER (*Ber.*, 1906, **39**, 19—26).—When α-methylmorphimethine is heated in a vacuum, it changes to a violet liquid, which then assumes a clear yellow colour; if the temperature is then suddenly raised, a yellow oil distils at 220—240° under 12 mm. pressure, consisting of the β-isomeride previously prepared by the action of alcoholic potash (Knorr and Smiles, Abstr., 1902, i, 817); its identity was confirmed by preparing the benzoate and the methiodide.

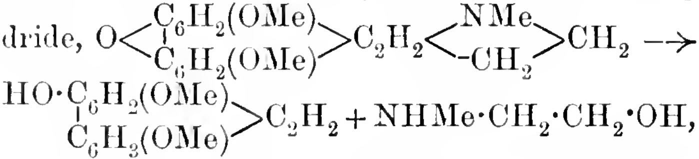
α-Methylmorphimethine separates from dilute alcohol in crystals belonging to the sphenoidal-rhombic system [$a:b:c = 0·7265:1:0·5142$], which exhibit rotatory polarisation in the solid state as well as in solution. The β-isomeride crystallises in the same system [$a:b:c = 0·5832:1:0·9560$].

α-Ethylthiocodide also crystallises in the same system [$a:b:c = 0·7481:1:0·7659$]. T. M. L.

Resolution of Thebaine by Benzoyl Chloride. ROBERT PSCHORR and W. HAAS (*Ber.*, 1906, **39**, 16—19).—*Benzoylthebaol*, $C_{23}H_{18}O_4$, prepared by the action of benzoyl chloride on thebaine at 0°, crystallises from acetic acid in thin, colourless needles and melts at 160—161°. The *dibromo*-derivative, $C_{23}H_{16}O_4Br_2$, crystallises from acetic acid in long needles and melts at 229°.

Benzoylthebaolquinone, $C_{23}H_{16}O_6$, prepared by oxidation with chromic acid, separates from acetic acid in yellow crystals and melts at 216°; it is hydrolysed by sodium ethoxide to Freund's thebaolquinone.

The basic product of the action of benzoyl chloride was identified by means of its aurichloride, $C_3H_{10}ONAuCl_4$, as ethoxymethylamine. The decomposition is thus essentially similar to that brought about by acetic anhydride,



$$O<\begin{matrix}C_6H_2(OMe)\\ |\\ C_6H_2(OMe)\end{matrix}>C_2H_2<\begin{matrix}NMe\\ \text{-}CH_2\end{matrix}>CH_2 \longrightarrow$$

$$\begin{matrix}HO\cdot C_6H_2(OMe)\\ |\\ C_6H_3(OMe)\end{matrix}>C_2H_2 + NHMe\cdot CH_2\cdot CH_2\cdot OH,$$

and involves the resolution of a furan ring and of a nitrogen ring and the separation of a carbon to carbon linking. T. M. L.

Hordenine: a New Alkaloid obtained from Malt Germs. EUGÈNE LÉGER (*Compt. rend.*, 1906, **142**, 108—110).—*Hordenine*, $C_{10}H_{15}ON$, a new alkaloid extracted by Stas' method from malt germs, forms colourless, voluminous, strongly doubly refracting orthorhombic prisms [$a:b:c = 0·5257:1:0·3551$ (Wyrouboff)]. It melts at 117·8° (corr.), sublimes like camphor at 140—150°, dissolves readily in alcohol, chloroform, or ether, forming optically inactive solutions, is sparingly soluble in benzene, and is almost insoluble in toluene, xylene, or light petroleum.

Hordenine is alkaline towards litmus or phenolphthalein, liberates ammonia from its salts, and is not attacked by concentrated sulphuric acid or by potassium hydroxide, either fused or in aqueous solution. It reduces acid solutions of potassium permanganate, ammoniacal solutions of silver nitrate or iodic acid, and forms soluble salts with acids; the *sulphate*, $(C_{10}H_{15}ON)_2,H_2SO_4,H_2O$, crystallises in brilliant, prismatic needles, readily soluble in water, sparingly so in alcohol; the *hydrochloride*, $C_{10}H_{15}ON,HCl$, crystallises from alcohol in thin needles; the *hydrobromide*, $C_{10}H_{15}ON,HBr$, forms brilliant, long, prismatic needles, readily soluble in water, less so in alcohol; the *hydriodide*,

$$C_{10}H_{15}ON,HI,$$

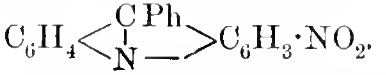
crystallises in long prisms slightly less soluble than the preceding salt.

Hordenine is a tertiary base and yields a *methiodide*,

$$C_{10}H_{15}ON,MeI,$$

which crystallises from water in colourless prisms; it contains a phenolic hydroxyl group and reacts with acetic anhydride to form a syrupy *acetyl* derivative, which is basic and forms *acetylhordenine hydriodide*, $C_{10}H_{14}ONAc,HI$, crystallising from alcohol or water in yellowish-white, tabular crystals. M. A. W.

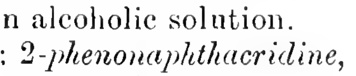
New Synthesis of Phenylacridine Derivatives. FRITZ ULLMANN and HANS W. ERNST (*Ber.*, 1906, **36**, 298—310).—5-*Nitro-2-anilinobenzophenone*, $NHPh\cdot C_6H_3(NO_2)\cdot COPh$, prepared by heating aniline with 2-chloro-5-nitrobenzophenone and potassium carbonate for three hours at 180°, crystallises from alcohol, melts at 155°, and by heating with glacial acetic acid containing a little concentrated sulphuric acid is converted into 3-*nitro-5-phenylacridine*,



$$C_6H_4{<}\begin{matrix}CPh\\ |\\ N\end{matrix}{>}C_6H_3\cdot NO_2.$$

This can also be prepared directly from 2-chloro-5-nitrobenzophenone by heating the latter with aniline and sodium acetate at 150°; it crystallises from alcohol in intensely yellow needles and melts at 209°. On reduction, 3-amino-5-phenylacridine is obtained; Hess and Bernthsen (Abstr., 1885, 800) describe this substance and its salts as resinous in character, but by the authors' method the *base* is obtained on crystallising from alcohol in the form of slender, yellow needles which melt at 200°; the *hydrochloride* crystallises in large needles with a bronze-like lustre and in alcoholic solution shows a green fluorescence. 3-*Acetylamino-5-phenylacridine* crystallises from benzene, melts at 256°, and also shows a green fluorescence in alcoholic solution.

9-*Nitro-7-phenyl*-1 : 2-*phenonaphthacridine*,



$$C_{10}H_6{<}\begin{matrix}CPh\\ |\\ N\end{matrix}{>}C_6H_3\cdot NO_2,$$

prepared by heating together 2-chloro-5-nitrobenzophenone and β-naphthylamine in nitrobenzene solution at 205°, crystallises from glacial acetic acid in straw-coloured needles, melts at 274°, and on reduction gives 9-*amino-7-phenyl*-1 : 2-*phenonaphthacridine*; this crystallises from alcohol in dark yellow prisms, melts at 282°, and gives a *hydrochloride* crystallising in red needles, which become yellow when heated with water.

9-*Nitro-7-phenyl*-2 : 1-*phenonaphthacridine*, prepared by heating 2-chloro-5-nitrobenzophenone with alcoholic α-naphthylamine for five hours at 150—170°, crystallises from glacial acetic acid in yellow needles and melts at 264°.

9-Amino-7-phenyl-2 : 1-phenonaphthacridine, crystallises from alcohol in stellate aggregates of brown needles, melts at 224°, and gives a red *hydrochloride*.

3-Nitro-7-amino-5-phenylacridine,

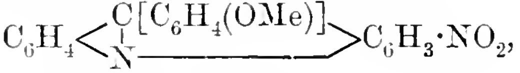
$$NO_2\cdot C_6H_3{<}\substack{CPh\\|\\N}{>}C_6H_3\cdot NH_2,$$

prepared by heating 2-chloro-5-nitrobenzophenone with *p*-phenylenediamine for three-quarters of an hour at 200°, crystallises from benzene in garnet-coloured needles and melts at about 181° ; the *hydrochloride* forms yellowish-brown needles. On reduction, 3 : *7-diamino-5-phenylacridine* is obtained, which crystallises from benzene in lemon-yellow needles ; the *picrate*, $C_{19}H_{15}N_3,C_6H_3O_7N_3$, forms purplish-red needles.

2-Chloro-5-nitro-4′-methoxybenzophenone,

$$NO_2\cdot C_6H_3Cl\cdot CO\cdot C_6H_4\cdot OMe,$$

prepared from 2-chloro-4-nitrobenzoyl chloride and anisole by the Friedel-Crafts reaction, crystallises from benzene on adding light petroleum in colourless needles and melts at 105°. On heating it with aniline and powdered potassium carbonate at 180°, *5-nitro-2-anilino-4′-methoxybenzophenone*, $NHPh\cdot C_6H_3(NO_2)\cdot CO\cdot C_6H_4\cdot OMe$, is obtained ; it crystallises from alcohol in yellow needles or plates, melts at 144—155°, and when heated with glacial acetic acid containing sulphuric acid is converted into *3-nitro-5-p-methoxyphenylacridine*,



$$C_6H_4{<}\substack{C[C_6H_4(OMe)]\\|\\N}{>}C_6H_3\cdot NO_2,$$

which crystallises from alcohol and melts at 178°.

2-o-Methoxyanilino-5-nitrobenzophenone,

$$OMe\cdot C_6H_4\cdot NH\cdot C_6H_3(NO_2)\cdot COPh,$$

prepared by heating 2-chloro-5-nitrobenzophenone with *o*-anisidine and potassium carbonate at 215°, crystallises from alcohol either in bright yellow needles sparingly soluble in the solvent or more soluble greenish-yellow leaflets ; the two forms melt at 139° and are interconvertible. *3-Nitro-9-methoxy-5-phenylacridine*, prepared by heating together the same substances in the absence of potassium carbonate or by heating 5-nitro-2-*o*-methoxyanilinobenzophenone with concentrated sulphuric acid, crystallises from alcohol in orange-yellow needles and melts at 285°.

W. A. D.

Nature of Oxazine and Thiazine Dyes. ARTHUR HANTZSCH (*Ber.*, 1906, **39**, 153—159. Compare Abstr., 1905, i, 605).—Largely polemical in reply to Kehrmann (*ibid.*, i, 670). The ammonium quinonoid constitutional formulæ are regarded as being more in harmony with known facts than are Kehrmann's oxonium or thiazonium formulæ. Bernthsen's methylene-azure (O. Fischer, *Ber.*, 1905, **38**, 3435) has been examined, and in solution its salts behave as neutral salts and are comparable with the aromatic quaternary ammonium salts. The azure-blue colour of the solution persists for a long time after the addition of sodium acetate or carbonate. This would not be probable if the compound contained the group $\geqslant SO\cdot Cl$.

J. J. S.

Arylhydantoins. Gustav Frerichs and M. Hollmann (*Arch. Pharm.*, 1905, **243**, 684—710. Compare Abstr., 1899, i, 806; 1903, i, 16).—Substituted aminopropionylcarbamides,

$$NH_2·CO·NH·CO·CHMe·NH·C_6H_4R$$

[R = H or Me], were prepared by heating α-bromopropionylcarbamide, $NH_2·CO·NH·CO·CHMeBr$ (H. Frerichs, *Arch. Pharm.*, 1903, **241**, 195), with an arylamine, $NH_2·C_6H_4R$, in alcoholic solution. By heating the same mixture, without the addition of alcohol, to a higher temperature, or by heating the products just mentioned above their melting points, substituted α-methyl-β-arylhydantoins were prepared, and by heating these with alkyl iodides, R^1I, and alcoholic potassium hydroxide, α-methyl-β-aryl-γ-alkylhydantoins,

$$CO<\begin{matrix}N(C_6H_4R)·CHMe\\ NR^1——CO\end{matrix},$$

were obtained (the allyl derivatives united with hydrogen bromide or bromine in acetic acid solution, forming bromo- and dibromo-propyl derivatives). Similar condensations took place with chloroacetic acid and with chloroacetamide; with ethylene bromide, 2 molecules of the hydantoins condensed. α-Methyl-β-phenylhydantoin was prepared not only by the method given above, but also by heating with alcoholic potassium hydroxide, *α-bromopropionylphenylcarbamide*, melting at 158°, which was obtained by mixing α-bromopropionyl bromide with phenylcarbamide in ethereal solution.

The other new substances described are enumerated below; the numbers indicate melting points.

Propionylcarbamides. *α-Anilino-*, 143°; *α-toluidino-*, *o* 160°, *m* 156°, *p* 160°.

α-Methylhydantoins. *β-Phenyl-*, 146°; *β-tolyl-*, *o* 167°, *m* 137°, *p* 173°. Derivatives of these in this order: *γ-methyl*, 128°, 114°, 89°, 96°; *γ-ethyl*, 114°, liquid, 76°, 86°; *γ-allyl*, 88°, liquid, 58°, 96°; *γ-bromopropyl*, 89°, liquid, 92°, 85°; *γ-dibromopropyl*, 137° (*monobromo*-substitution derivative of this, 148°; obtained by the action of bromine in acetic acid solution), 104°, 85°, 101°; *γ-acetic acid*, 163°, 182°, 148°, 179° (*barium* salts crystallise with 3, 3, 2, $2H_2O$); *γ-acetamide*, 225°, 166°, 159°, 205°; *γ-ethylene* (di-), 200°, liquid, liquid, 173°.

C. F. B.

Constitution of the Cyanine Dyes. W. König (*J. pr. Chem.*, 1906, [ii], **73**, 100—108. Compare Miethe and Book, Abstr., 1904, i, 622, 776; Book, this vol., i, 42).—As no case is known where a methyl group in the 2- or 3-position in pyridine or quinoline retains its property of condensing with aldehydes and ketones when the ring is reduced wholly or partially, it is probable that the cyanine dyes contain 2 atoms of hydrogen less than shown in Miethe and Book's formula (*loc. cit.*), ethyl-red having the structure

$$\begin{matrix}CH{=}CH\\ |\\ NEt·C_6H_4\end{matrix}>C{:}CH·C\begin{matrix}\diagup CH{=}CH\\ \qquad\quad |\\ \diagdown\!\!= NEtI·C_6H_4\end{matrix},$$

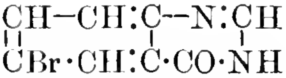
and the blue diethylcyanine,

$$\begin{matrix}CH{=}CH\\ |\\ NEt·C_6H_4\end{matrix}>C{:}CH·C\begin{matrix}\diagup\!\!= CH—CH\\ \qquad\quad ||\\ \diagdown C_6H_4·NEtI\end{matrix}.$$

These formulæ are used to explain the similarity of the cyanine dyes and the pyridine dyes obtained from furfuraldehyde (König, this vol., i, 109). Contrary to the view of Miethe and Book (*loc. cit.*), the additive compounds with iodine are considered to be periodides, as they are not lighter in colour than the parent dyes, as would be the case if the addition took place to an ethylene linking. G. Y.

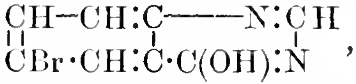
Preparation of 6-Bromo-4-ketodihydroquinazolines from 5-Bromo-2-aminobenzoic Acid and certain of its Derivatives.

MARSTON T. BOGERT and WILLIAM F. HAND (*J. Amer. Chem. Soc.*, 1906, **28**, 94—104. Compare Abstr., 1904, i, 108).—Quinazolines have been prepared by the following methods. I. From 5-bromo-2-aminobenzoic acid: (1) by heating the acid with an acid anhydride or a nitrile in a sealed tube at 230—250°; this method gives a poor yield and an impure product; (2) by heating the acid or its ammonium salt with acid amides, a method which gives excellent results with formamide, but less satisfactory results with acetamide, and is not applicable to the higher amides; (3) by heating the acid with excess of glacial formic acid or an acid anhydride and afterwards adding excess of ammonium carbonate and continuing the heating; good yields are generally obtained in this way, and the products can be easily purified. II. By heating ammonium 5-bromo-2-acetylaminobenzoate, when a nearly quantitative yield is obtained. III. From 5-bromo-2-acetylaminobenzonitrile: (1) by warming it with solution of alkali dioxide; this method gives a quantitative yield of the pure substance; (2) by boiling it with concentrated hydrochloric acid. IV. By the action of primary amines on 5-bromo-2-acetylanthranil. The following quinazolines are described.

6-*Bromo-4-ketodihydroquinazoline*, 

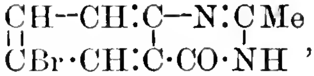
$$\begin{array}{l}\mathrm{CH{-}CH{:}C{-}N{:}CH} \\ \mathrm{CBr{\cdot}CH{:}C{\cdot}CO{\cdot}NH}\end{array}$$

or



$$\begin{array}{l}\mathrm{CH{-}CH{:}C{-\!-\!-}N{:}CH} \\ \mathrm{CBr{\cdot}CH{:}C{\cdot}C(OH){:}N}\end{array},$$

crystallises in transparent, six-sided prisms, melts at 272—273° (corr.), and is soluble in alcohol, acetone, or aniline; its *platinichloride* forms short, thick prisms.

6-*Bromo-4-keto-2-methyldihydroquinazoline*, 

$$\begin{array}{l}\mathrm{CH{-}CH{:}C{-}N{:}CMe} \\ \mathrm{CBr{\cdot}CH{:}C{\cdot}CO{\cdot}NH}\end{array},$$

crystallises in colourless needles, decomposes when slowly heated, but melts at 298—300° (corr.) if rapidly heated, is easily soluble in hot acetone or hot aniline, and moderately so in hot alcohol; its hydrochloride is instantly dissociated by water.

6-*Bromo-4-keto-2-ethyldihydroquinazoline* forms slender, prismatic needles, softens at 263°, melts at 267—268·5° (corr.), and behaves towards solvents like the methyl homologue.

6-*Bromo-4-keto-2-*iso*propyldihydroquinazoline* crystallises in colourless, prismatic needles, and, when rapidly heated, melts at 259—260·5° (corr.).

6-*Bromo-4-keto-2-*iso*butyldihydroquinazoline* forms small, prismatic needles, softens at 250°, and melts and decomposes slightly at 253—254° (corr.).

6-*Bromo-4-keto-2-*iso*amyldihydroquinazoline* crystallises in prismatic needles, melts at 235—236° (corr.), is easily soluble in hot aniline, and moderately so in hot alcohol.

6-*Bromo-4-keto-3-phenyl-2-methyldihydroquinazoline* crystallises from alcohol in colourless, six-sided prisms and melts at 185—186° (corr.).

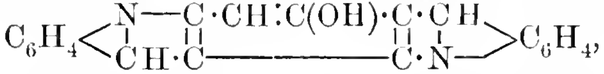
6-*Bromo-4-keto-3-o-tolyl-2-methyldihydroquinazoline* forms colourless crystals and melts at 137—138° (corr.).

Attention is drawn to the fact that with the exception of the methyl derivative, the melting points of these quinazolines fall regularly as the molecular weight increases, and that those of the *iso*-compounds are higher than those of the corresponding *n*-compounds. E. G.

Quinazoline Alkyl Haloids. SIEGMUND GABRIEL and JAMES COLMAN (D.R.-P. 161401).—Quinazoline-3-methylium hydroxide (Abstr., 1904, i, 1060) dissolves in concentrated hydrochloric acid to form the *chloride* melting at 171—172°. The *bromide* dissolves in water and melts at 150—152°. The *hydroxide* prepared from quinazoline ethiodide is insoluble in cold water, but dissolves in hot water and melts at 145—146°; the *chloride* melts at 150—151°. The salts find therapeutic application. C. H. D.

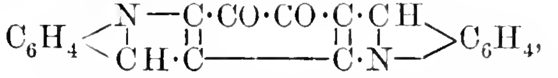
Hydroxyquinacridine and Phloroquinyl. STEFAN VON NIEMENTOWSKI (*Ber.*, 1906, **39**, 385—392. Compare Abstr., 1896, i, 261; Eliasberg and Friedländer, Abstr., 1892, 1106).—When heated to 115—120°, a mixture of 2 mols. of *o*-aminobenzaldehyde and 1 mol. of phloroglucinol develops heat and forms hydroxy-β-quinacridine together with small amounts of dihydroxyacridine and of phloroquinyl, which is formed as the chief product of the interaction of 3 mols. of *o*-aminobenzaldehyde with 1 mol. of phloroglucinol.

4-*Hydroxy-β-quinacridine* (4-*keto*-3 : 4-*dihydro-β-quinacridine*),



$$C_6H_4<\begin{matrix}N—C\cdot CH\colon C(OH)\cdot C\cdot CH\\ CH\cdot C————C\cdot N\end{matrix}>C_6H_4,$$

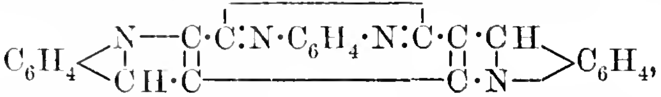
crystallises from glacial acetic acid in glistening, black needles containing $3C_2H_4O_2$, which is lost at 125°; it melts at 360°, is readily soluble in boiling glacial acetic acid, but only sparingly so in water, chloroform, carbon tetrachloride, or benzene, forming brownish-yellow, or in alcohol, ether, or acetone, emerald-green, solutions; the solution in nitrobenzene is brownish-yellow, and becomes emerald-green when heated. It is only very sparingly soluble in aqueous ammonia, alkali hydroxides, or dilute acids, but dissolves in concentrated sulphuric acid to form a green solution having a slight fluorescence. 4-*Acetoxy-β-quinacridine*, $C_{20}H_{11}ON_2Ac$, crystallises from nitrobenzene in slender, glistening, almost black needles with steel-blue lustre and melts at 300°. When oxidised with sodium dichromate in boiling glacial acetic acid solution, 4-hydroxy-β-quinacridine yields 3 : 4-*diketo*-3 : 4-*dihydro-β-quinacridine*,



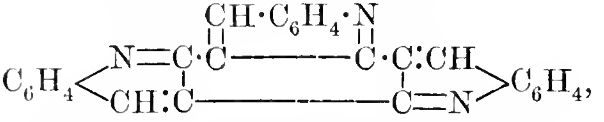
$$C_6H_4<\begin{matrix}N—C\cdot CO\cdot CO\cdot C\cdot CH\\ CH\cdot C———C\cdot N\end{matrix}>C_6H_4,$$

which crystallises in long, golden-yellow leaflets, becomes black and melts about 410°, and dissolves in concentrated sulphuric acid to form a golden-yellow solution, or in boiling methyl alcohol containing a drop of concentrated aqueous potassium hydroxide solution, forming a dark-coloured solution; this does not change in colour when shaken with air (compare Bamberger, Abstr., 1885, 807).

When heated with *o*-phenylenediamine in glacial acetic acid solution, diketoquinacridine yields *β-quinacrid*-3 : 4-*azine*,



which crystallises from nitrobenzene in yellow needles, melts, becomes black, and forms a crystalline sublimate at 420°, and is only sparingly soluble in the ordinary solvents, but dissolves in concentrated sulphuric or hydrochloric acid to form a yellow solution; it forms a crystalline *hydrochloride*, *platinichloride*, and *aurichloride*.

Phloroquinyl,  crystallises from nitrobenzene in yellow or light brown needles, melts at 403°, is moderately soluble in boiling nitrobenzene, but is only sparingly so or is insoluble in other organic solvents, and is insoluble in dilute alkali hydroxides or acids, but dissolves in concentrated sulphuric acid, forming a yellow solution. It remains unchanged when heated with concentrated hydrochloric acid in a sealed tube at 200°, or when distilled over zinc dust, or when treated with sodium amalgam. It forms a red *nitro*-derivative when boiled with concentrated nitric acid, *additive* and *substitution* products when acted on by bromine with, or in the absence of, a solvent, and an unstable *additive*-compound with methyl sulphate, which yields the phloroquinyl when boiled with aqueous potassium hydroxide.

G. Y.

Oxidation Products of *o*-Aminophenols. FRIEDRICH KEHRMANN (*Ber.*, 1906, 39, 134—138).—[With M. MATTISSON.]—Air is passed through a hot aqueous solution of *o*-aminophenol until the amount of precipitate no longer increases, and the product removed, dried, and extracted with boiling benzene in the presence of animal charcoal. The benzene solution yields a mixture of two azine derivatives, which may be separated by acetylation and crystallisation of the acetyl derivatives from glacial acetic acid. The acetylaminophenoxazone, which is present in larger quantity, forms large, brownish-red plates and melts at 275°; the isomeric compound is less soluble, forms brick-red needles, and melts at 285°. Both acetyl derivatives are decomposed by 50 per cent. sulphuric acid, yielding, on the addition of water, brownish-blood-red solutions.

The solution from the compound melting at 285° reacts with nitrous acid with a brisk evolution of gas, but no indication of a precipitate. The isomeric compound under similar treatment yields no gas, but forms an orange-red *precipitate*, $C_{12}H_7O_3N_3$, which crystallises from a mixture of alcohol and benzene in yellowish-red needles decomposing at 175°.

[With W. URECH.]—When *o*-amino-*o*-cresol is oxidised in a similar manner, it yields orange-red, glistening crystals, $C_{14}H_{12}O_2N_2$, which separate from a mixture of alcohol and benzene as red prisms with a violet, metallic lustre. The *hydrochloride* forms brownish-black needles. With nitrous acid, an orange-coloured precipitate is obtained.

[With E. BÜHLER.]—*o*-Amino-*m*-cresol yields orange-red crystals, C_7H_7ON, with a blue fluorescence; they melt at 176° and dissolve sparingly in water, but readily in organic solvents. The compound is decidedly basic; the *hydrochloride*, $(C_7H_7ON)_2,HCl$, forms brown crystals; the *platinichloride* is insoluble in water and forms brownish-red crystals; the *dichromate*, $C_{28}H_{30}O_4N_4Cr_2O_7$, forms red crystals; the *nitrate*, $C_{14}H_{15}O_2N_2NO_3$, forms red needles which dissolve readily in water. The base cannot be reduced readily. J. J. S.

Chemical and Thermochemical Researches on the Constitution of the Rosanilines. JULES SCHMIDLIN (*Ann. Chim. Phys.*, 1906, [viii], 7, 195—279).—A *résumé* of work already published in Abstr., 1903, i, 687; ii, 530, 633; 1904, i, 698, 785, 943, 944, 945, 1061; 1905, i, 75, and ii, 11 and 12. T. A. H.

Indamines and Thiazines. ROBERT GNEHM and W. SCHRÖTER (*J. pr. Chem.*, 1906, [ii], 73, 1—20. Compare Gnehm, Bot, and Weber, Abstr., 1902, i, 831; Gnehm and Bot, Abstr., 1904, i, 451; Gnehm and Weber, *ibid.*, 532; Gnehm and Kaufler, *ibid.*, 687, 935).—*p*-Amino-derivatives of methyl- and ethyl-anilines and of methyl- and ethyl-*o*-toluidines are prepared by formation of the nitrosoamines, conversion of these into the *p*-nitroso-derivatives by means of alcoholic hydrochloric acid and ether in the case of the aniline derivatives, or of concentrated aqueous hydrochloric acid with the derivatives of *o*-toluidine, and reduction of the nitroso-compounds with zinc and hydrochloric acid.

p-*Aminomethyl*-o-*toluidine*, $NH_2·C_6H_3Me·NHMe$, is obtained as a colourless, viscid oil which does not solidify at −20°, boils at 276—276·5° (corr.), and becomes brown owing to oxidation when exposed to the air. The *sulphate*, $(C_8H_{12}N_2)_2,H_2SO_4$, crystallises from dilute alcohol in slender, white needles.

s-*Di*-p-*methylaminodiphenylamine*, $NH(C_6H_4·NHMe)_2$, is formed by oxidation with aqueous sodium hypochlorite of a mixture of methylaniline and *p*-phenylenemethyldiamine, and reduction of the resulting solution with zinc dust. It crystallises in glistening, colourless leaflets or needles, melts at 115° (corr.), is easily soluble in chloroform or acetone, but less so in ether, alcohol, benzene, toluene, or hot light petroleum, and when moist is oxidised rapidly by the air, becoming yellow to brownish-blue. The *hydrochloride*, $C_{14}H_{17}N_3,2HCl$, forms brown leaflets, froths at 220°, and melts at 225—227° (corr.). The *triacetyl* derivative, $C_{14}H_{14}N_3Ac_3$, melts at 245° (corr.).

Di-p-*ethylaminodiphenylamine*, $NH(C_6H_4·NHEt)_2$, formed from ethylaniline and *p*-phenylene-ethyldiamine, melts at 95° (corr.) and is more readily soluble than the *s*-dimethyl compound. The *hydrochloride*, $C_{16}H_{21}N_3,2HCl$, melts at 217—218° (corr.). The *triacetyl* derivative, $C_{16}H_{18}N_3Ac_3$, melts at 207° (corr.).

As they undergo oxidation with great ease, the *s*-dialkyl-leucindamines, formed from ethyl-*o*-toluidine and ethyl-*p*-tolylenediamine and from methyl-*o*-toluidine and methyl-*p*-tolylenediamine, cannot be isolated except in the form of salts or derivatives.

*Di-*p*-ethylaminoditolylamine hydriodide*,

$$NH(C_6H_3Me\cdot NHEt)_2,3HI,2H_2O,$$

crystallises in glistening, orange leaflets and melts at 120—122° (corr.). The *tribenzoyl* derivative, $C_{18}H_{22}N_3Bz_3$, formed by the action of benzoyl chloride and sodium hydroxide on the hydriodide, is obtained as a white, glutinous powder, which becomes soft at 60° and melts above 90°.

*Di-*p*-methylaminoditolylamine hydriodide*, $NH(C_6H_3Me\cdot NHMe)_2,2HI$, crystallises in sheaves of slender, white needles and melts at 242°. The *tribenzoyl* derivative, $C_{16}H_{18}N_3Bz_3$, resembles that of the *s*-diethyl compound.

*Trinitrophenyl-*p*-phenylenemethyldiamine*,

$$NHMe\cdot C_6H_4\cdot NH\cdot C_6H_2(NO_2)_3,$$

is formed by boiling *p*-phenylenemethyldiamine with picryl chloride and potassium acetate in alcoholic solution in a reflux apparatus; it crystallises in dark brownish-red, glistening leaflets, melts at 188° (corr.), and when condensed with sulphur chloride in presence of potassium acetate yields a mixture of *products* from which no one could be isolated.

*Dinitrophenyl-*p*-phenylenemethyldiamine*,

$$NHMe\cdot C_6H_4\cdot NH\cdot C_6H_3(NO_2)_2,$$

formed from *p*-phenylenemethyldiamine and 1-chloro-2 : 4-dinitrobenzene, melts at 153°.

The action of sulphur chloride on di-*p*-ethyldiaminodiphenylamine in benzene solution leads to the formation of a labile additive *compound*, which is obtained as a green precipitate, becoming greyish-green on drying.

Tolylenemethyldiaminethiosulphonic acid,

$$NH_2\cdot C_6H_2Me(NHMe)\cdot S_2O_3H$$

[$Me : NHMe : S_2O_3H : NH_2 = 1 : 2 : 4 : 5$], is formed by adding acetic acid and potassium dichromate to a mixture of *p*-methylamino-*o*-toluidine sulphate, aluminium sulphate, and sodium thiosulphate in aqueous solution. It forms green crystals, melts at 212—213°, and when oxidised with sodium hypochlorite in dilute aqueous sodium carbonate solution yields a *product* which may be the thiazine,

$$\begin{array}{l} CMe\text{———}CH\!:\!C\cdot N\!:\!C\cdot C(ONa)\!:\!CH \\ C(NHMe)\cdot CH\!:\!C\text{–}S\text{–}C\!:\!CH\text{——}C\!:\!NH \end{array}$$

Aminoleucomethylene-blue, $C_{16}H_{20}N_4S$, is formed by reduction of methylene-green (nitromethylene-blue) with zinc dust and acetic acid. It crystallises in sheaves of slightly green needles, melts at 143—145°, and is very easily oxidised, so that it can be obtained only with complete exclusion of air. G. Y.

Phenylcarbamidodiphenylmethenylamidine and its easy Decomposition with Formation of Phenylcarbimide. REINHOLD VON WALTHER (*J. pr. Chem.*, 1906, [ii], **73**, 108—112).—*Phenylcarbamidodiphenylmethenylamidine*, $NHPh\cdot CO\cdot NPh\cdot CH\!:\!NPh$, is formed when diphenylmethenylamidine is heated with phenylcarbimide on the water-bath. It crystallises from light petroleum in small, stout, transparent prisms, melts at 104°, and is readily soluble in the ordinary solvents when warm. *s*-Diphenylcarbamide melts at 235°, and diphenylmethylcarbamide at 104°. A table is given to show that the introduction of aliphatic groups into phenyl- or *s*-diphenylcarbamide depresses the melting point, the ethyl group effecting the fusibility to a greater extent than the methyl group, and that the melting point rises again slowly as successive methyl groups are introduced.

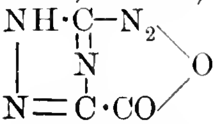
Phenylcarbamidodiphenylmethenylamidine decomposes slowly at the laboratory temperature with formation of *s*-diphenylcarbamide, or quickly when boiled with alcohol, with formation of diphenylmethenylamidine and ethyl phenylcarbamate; it interacts with aniline with development of heat and formation of *s*-diphenylcarbamide, or with *p*-chloroaniline to form *p*-chloro-*s*-diphenylcarbamide.

p-*Chlorophenylcarbamidodiphenylmethenylamidine*,

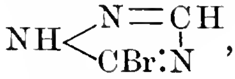
$$C_6H_4Cl\cdot NH\cdot CO\cdot NPh\cdot CH{:}NPh,$$

formed from diphenylmethenylamidine and *p*-chlorophenylcarbimide, crystallises from light petroleum in white, prismatic needles, melts at 97—103°, and interacts with aniline to form *p*-chloro-*s*-diphenylcarbamide, or with *p*-chloroaniline to form *s*-di-*p*-chlorophenylcarbamide.

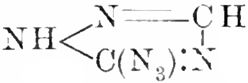
Diphenylmethylcarbamide and complex carbamides, such as 1-phenylcarbamido-2-methylindole, do not interact with aniline at the laboratory temperature. G. Y.

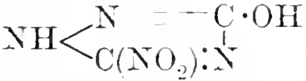
Derivatives of Triazole. WILHELM MANCHOT and R. NOLL (*Annalen*, 1905, **343**, 1—27).—The constitution for diazotriazolecarboxylic acid,  $\left.\begin{array}{l} NH\cdot C{-}N_2 \\ |\quad\;\; \| \\ |\quad\;\; N \\ |\quad\;\; | \\ N{=}C\cdot CO \end{array}\right> O,H_2O$, suggested by Thiele and Manchot (Abstr., 1899, i, 167), represents the compound as an internal anhydride. Since, however, the ester of aminotriazolecarboxylic acid yields an analogous diazo-compound, which is obviously unable to form such an anhydride, it is more probable that the acid above mentioned is represented by the formula  $NH<\begin{array}{l} N \qquad\quad C\cdot CO_2H \\ C(NH\cdot NO){:}N \end{array}$.

Diazotriazolecarboxylic acid is best prepared by adding to sodium aminotriazolecarboxylate, first, concentrated hydrochloric acid, and then at −4° a solution of sodium nitrite. The *ethyl* ester is prepared in a similar manner by diazotising ethyl aminotriazolecarboxylate; it is very explosive.

It is to be noted that chlorotriazole (*loc. cit.*) does not lose chlorine when treated either with nascent hydrogen or nitric acid. *Bromotriazole*,  $NH<\begin{array}{l} N{=}CH \\ CBr{:}N \end{array}$, is prepared by pouring fuming hydrobromic acid over the diazo-acid rubbed up with a little water; it crystallises in prisms melting at 188—189°, and by sodium amalgam is converted into triazole. With silver nitrate it gives a white, and with copper acetate a pale blue, precipitate. Diazotriazolecarboxylic acid reacts with aqueous potassium iodide, iodine being set free and triazole and *iodotriazole* formed. The latter crystallises in needles melting and decomposing at 208°, iodine being liberated; with silver nitrate and copper acetate, it gives precipitates similar to those formed from the bromotriazole, and by sodium amalgam it is reduced to triazole.

Hydroxytriazolecarboxylic acid (Abstr., 1899, i, 84) can be obtained from the diazo-acid and acetic acid; at first orange-red needles of the anhydrous acid are formed, which gradually pass into the crystals of the hydrated acid. When reduced at a low temperature with stannous chloride and hydrochloric acid, diazotriazolecarboxylic acid is converted into *triazylhydrazine*,  $\mathrm{NH}<\begin{array}{l}\mathrm{N}=\!=\!=\mathrm{CH}\\ \mathrm{C(N_2H_3){:}N}\end{array}$, the *hydrochloride* of which crystallises in needles melting and decomposing at 224°. The *picrate* crystallises in pale yellow needles melting at 165°. *Benzylidenetriazylhydrazone* crystallises in needles melting at 225·5—226°; the corresponding *salicyl* derivative melts and decomposes at 259°; the *acetophenone* derivative forms small plates, melting at 276°, and the *acetone* derivative melts at 216°.

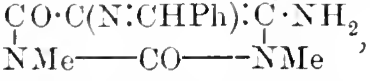
Triazylazoimide,  $\mathrm{NH}<\begin{array}{l}\mathrm{N}=\!=\mathrm{CH}\\ \mathrm{C(N_3){:}N}\end{array}$, prepared from the hydrazine hydrochloride and sodium nitrite, forms crystals melting at 121—122° and yields an explosive *silver* salt.

Nitrohydroxytriazole,  $\mathrm{NH}<\begin{array}{l}\mathrm{N}=\!=\!=\mathrm{C\cdot OH}\\ \mathrm{C(NO_2){:}N}\end{array}$, prepared when hydroxytriazole is treated with fuming nitric acid, forms crystals decomposing at 254°; its *silver* salt is a pale yellow, crystalline precipitate exploding when heated. When nitrohydroxytriazole is reduced with tin and hydrochloric acid, the corresponding *aminohydroxytriazole* is produced. Its *hydrochloride* is crystalline and melts at 196°, and the *picrate* crystallises in pale yellow needles melting at 204°; the *silver* salt is red, and gives a silver mirror when heated. K. J. P. O.

Preparation of 4 : 5-Diamino-2 : 6-dihydroxypyrimidine and its Derivatives. EMANUEL MERCK (D.R.-P. 161493).—5-*iso*Nitroso-4-amino-2 : 6-dihydroxy-3-methylpyrimidine (Traube, Abstr., 1900, i, 416; 1901, i, 54) may be reduced to 4 : 5-diamino-2 : 6-dihydroxy-3-methylpyrimidine in sulphuric acid solution by means of iron or zinc dust. Ammonia precipitates the base in bright yellow needles from a hot solution of the sulphate. 4 : 5-Diamino-2 : 6-dihydroxypyrimidine and its 1 : 3-dimethyl derivative may be prepared in similar manner.

C. H. D.

Action of Aldehydes on *o*-Diamines of the Pyrimidine Series. WILHELM TRAUBE and WALTHER NITHACK (*Ber.*, 1906, **39**, 227—235. Compare Abstr., 1900, i, 416; 1901, i, 54; 1904, i, 632; Gabriel and Colman, Abstr., 1901, i, 427).—Benzaldehyde (1 mol.) when added to an aqueous solution of 4 : 5-diamino-2 : 6-dioxy-1 : 3-dimethylpyrimidine (1 mol.) causes the separation of the *benzylidene* compound,



$$\begin{array}{l}\mathrm{CO\cdot C(N{:}CHPh){:}C\cdot NH_2}\\ \mathrm{NMe{-\!-\!-}CO{-\!-\!-}NMe}\end{array},$$

which is easily hydrolysed by acids into its constituents. On heating this compound with a second molecular proportion of benzaldehyde, 8-phenyl-7-benzyl-1 : 3-dimethylxanthine is obtained. Oxidation of the benzylidene compound with ferric chloride produces 8-phenyltheophylline.

4-*Amino-5-benzylideneamino-2 : 6-dioxy-3-methylpyrimidine*, $C_{12}H_{12}O_2N_4$, crystallises from hot alcohol in delicate needles which melt and decompose at 274°. It is insoluble in water or cold alcohol and is hydrolysed into its constituents by mineral acids. Ammoniacal solutions of silver salts are vigorously reduced by it, and on evaporation with nitric acid a reddish-purple residue is obtained. The corresponding *hydroxybenzylidene* compound, obtained from salicylaldehyde, forms long, yellow needles.

8-*Phenyl-7-benzyl-3-methylxanthine*, $C_{19}H_{16}O_2N_4$, obtained by heating the benzylidene compound (1 mol.) described previously and benzaldehyde (1 mol.) at 180°, separates from alcohol in yellow crystals which are unaffected by boiling acids and dissolve in alkalis to a yellow solution from which acids reprecipitate the substance unchanged.

3-Methylxanthine is prepared by warming a solution of 4 : 5-diamino-2 : 6-dioxy-3-methylpyrimidine in acetic acid, adding a solution of formaldehyde, and subsequently oxidising the condensation product formed by means of ferric chloride. In all its properties and colour reactions, the substance is identical with the 3-methylxanthine obtained by E. Fischer (Abstr., 1898, i, 700) and by Traube (*loc. cit.*).

8-*Hydroxyphenyl-3-methylxanthine*, $C_{12}H_{10}O_3N_4$, is obtained like the preceding compound, employing salicylaldehyde in the place of formaldehyde. It separates from alcohol in colourless needles which do not possess reducing properties and are not acted on by acids. By evaporation with nitric acid, a yellow-coloured residue is formed.

3-*Methyl*-8-iso*butylxanthine*, $C_{10}H_{14}O_2N_4$, obtained in similar manner from valeraldehyde, separates from hot water in minute, colourless needles.

4-*Amino-5-benzylideneamino*-2 : 6-*dioxy*-1 : 3-*dimethylpyrimidine*, $C_{13}H_{14}O_2N_4$, separates from alcohol in orange-yellow needles which melt and decompose at 220°. It is hydrolysed by mineral acids and reduces ammoniacal solutions of silver salts.

8-*Phenyl-7-benzyl*-1 : 3-*dimethylxanthine*, $C_{20}H_{18}O_2N_4$, obtained by fusing the preceding compound with an equivalent quantity of benzaldehyde, has a bright yellow colour, melts and decomposes at 221°, and is unaffected by mineral acids.

8-*Phenyl*-1 : 3-*dimethylxanthine*, $C_{13}H_{12}O_2N_4$, obtained from the benzylidene compound by oxidation with ferric chloride, crystallises from acetic acid in colourless, rhombic plates, insoluble in water or alcohol, and remains unchanged at 300°. It does not possess reducing properties and is practically unaffected by acids.

8-*Hydroxyphenyl-7-hydroxybenzyl*-1 : 3-*dimethylxanthine*, $C_{20}H_{18}O_4N_4$, obtained from the pyrimidine base and 2 mols. of salicylaldehyde at 180°, forms a yellow, crystalline powder. The intermediate *hydroxybenzylidene* compound (from 1 mol. of salicylaldehyde) crystallises in yellow needles which decompose at 242°.

1 : 3-*Dimethyl*-8-iso*butylxanthine*, $C_{11}H_{16}O_2N_4$, separates from hot aqueous solution in colourless needles melting at 227°. It is stable towards acids and does not possess reducing properties.

8-*Phenyl-7-benzylguanine*, $C_{18}H_{15}ON_5$, is obtained by heating at 180° 2 : 4 : 5-triamino-6-oxypyrimidine and benzaldehyde (2 mols.). It separates from hot alcohol in light yellow needles. The intermediate *benzylidene* compound (from 1 mol. of benzaldehyde) crystallises in yellow needles which melt and decompose at 276° and is easily hydrolysed by mineral acids. C. S.

Action of Phosphorus Oxychloride on Bispyrazolone Derivatives of Aldehydes and Ketones.

August Michaelis and Adalbert Zilg (*Ber.*, 1906, **39**, 370—381. Compare Abstr., 1905, i, 377, 392). — 4 : 4′-*Benzenyl*-1 : 3 : 5-*phenylmethylpyrazolone*-1′ : 3′-*phenylmethylpyrazole*,  $\begin{matrix}NPh\cdot CO\\ | \qquad\\ N—CMe\end{matrix}\!>\!C{:}CPh\cdot C\!<\!\begin{matrix}CH—NPh\\ \qquad | \\ CMe{:}N\end{matrix}$, is formed when benzylidenebis-1 : 3 : 5-phenylmethylpyrazolone (Lachowicz, Abstr., 1897, i, 119) is heated with phosphorus oxychloride at 135—140° and the product poured into water and treated with dilute sodium hydroxide. It crystallises from alcohol or ethyl acetate in slender, white needles, melts at 196°, has feeble basic properties, is readily soluble in hot alcohol, ethyl acetate, chloroform, ether, or benzene, and dissolves in concentrated hydrochloric acid, from which it separates unchanged on addition of water. The *platinichloride*,

$$C_{27}H_{22}ON_4,H_2PtCl_6,$$

forms slender, yellow needles and melts above 260°; the *aurichloride*, $C_{27}H_{22}ON_4,HAuCl_4$, crystallises in yellow needles and melts at 218°; the *methiodide*, $C_{27}H_{22}ON_4,2MeI,3H_2O$, crystallises from alcohol and forms a *periodide*, $C_{27}H_{22}ON_4,2MeI,I_3$. The *perbromide*,

$$C_{27}H_{20}ON_4Br_2,Br_3,$$

formed by the action of an excess of bromine on the base in glacial acetic acid solution, crystallises in yellow needles and when treated with hot dilute sodium hydroxide loses bromine and yields the *dibromide*, $C_{27}H_{20}ON_4Br_2$, which crystallises in slender needles and melts at 219°. The *nitro*-derivative, $C_{27}H_{21}ON_4\cdot NO_2$, formed by the action of fuming nitric acid on the base, crystallises from glacial acetic acid and melts at 235—243°.

4 : 4′-*Benzenylbis*-1 : 3 : 5-*phenylmethylpyrazolone*,

$$\begin{matrix}NPh-CO\\ | \qquad\\ N{=}CMe\end{matrix}\!>\!C{:}CPh\cdot CH\!<\!\begin{matrix}CO—NPh\\ \qquad | \\ CMe{:}N\end{matrix},$$

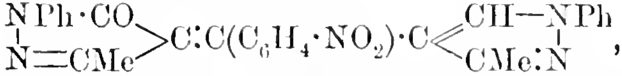
is formed by the action of phosphorus pentachloride on benzenylphenylmethylpyrazolonephenylmethylpyrazole at 140° or by oxidation of this with potassium permanganate and sulphuric acid below 30°. It crystallises in yellow needles, melts at 242°, and dissolves in aqueous alkali hydroxides to form a dark red solution, or in concentrated hydrochloric acid, from its solution in which it is precipitated on dilution with water. The ammonium and barium derivatives are red; the *silver* derivative, $C_{27}H_{21}O_2N_4Ag$, forms dark red, nodular crystals.

4 : 4′-p-*Chlorobenzenylbis*-1 : 3 : 5-*phenylmethylpyrazolone*,

$$C_{27}H_{23}O_2N_4Cl,$$

is formed by heating phenylmethylpyrazolone with *p*-chlorobenzaldehyde; it crystallises from alcohol in slender, white needles, melts and becomes red at 213°, and is readily soluble in alcohol, chloroform, dilute acids, or aqueous alkali hydroxides. When heated with phosphorus oxychloride in a sealed tube at 145° for ten hours, it yields 4 : 4′-p-*chlorobenzenyl*-1 : 3 : 5-*phenylmethylpyrazolone*-1 : 3-*phenylmethylpyrazole*,  $\left.\begin{array}{l}\mathrm{NPh\cdot CO}\\ \mathrm{N{=\!=}CMe}\end{array}\right>\mathrm{C{:}C(C_6H_4Cl)\cdot CH}<\begin{array}{l}\mathrm{CH{-}NPh}\\ \mathrm{CMe{:}N}\end{array}$, which crystallises in needles, melts at 213°, is insoluble in dilute aqueous alkali hydroxides, and when treated with phosphorus pentachloride yields a *product*, $C_{27}H_{21}O_2N_4Cl$. This crystallises in yellowish-red needles, sinters at 185°, and melts at 211°.

Phenylmethylpyrazolone condenses with *o*- and with *m*-nitrobenzaldehyde to form the corresponding *nitrobenzenylbisphenylmethylpyrazolones*, $C_{27}H_{23}O_4N_5$; these form yellowish-green crystals; the *m*-compound melts at 230°; the *o*-compound, which is readily soluble in benzene, melts at 226°. When heated with phosphorus oxychloride, the bispyrazolones form the corresponding *nitrobenzenylphenylmethylpyrazolonephenylmethylpyrazoles*,



$$\left.\begin{array}{l}\mathrm{NPh\cdot CO}\\ \mathrm{N{=\!=}CMe}\end{array}\right>\mathrm{C{:}C(C_6H_4\cdot NO_2)\cdot C}<\begin{array}{l}\mathrm{CH{-}NPh}\\ \mathrm{CMe{:}N}\end{array},$$

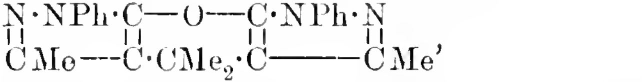
which are insoluble in aqueous alkali hydroxides. The *m*-compound forms colourless crystals and melts at 240°; the *o* compound forms green crystals and melts at 237°. When treated with phosphorus pentachloride, these substances yield *oxidation products*, $C_{27}H_{21}O_4N_5$, of which the *m*-derivative melts at 183° and the *o*-compound at 207°.

2 : 4 : 6-Trinitrobenzaldehyde does not condense with phenylmethylpyrazolone, but 2 : 5-dichloro-6-nitrobenzaldehyde interacts with the pyrazolone to form a mixture of 2 : 5-*dichloro*-6-*nitrobenzylidene*-1 : 3′ : 5-*phenylmethylpyrazolone*, $C_{10}H_8ON_2{:}CH\cdot C_6H_2Cl_2\cdot NO_2$, which crystallises in yellowish-red needles and melts at 139°, and 2 : 5-*dichloro*-6-*nitrobenzylidenebis*-1 : 3 : 5-*phenylmethylpyrazolone*,

$$NO_2\cdot C_6H_2Cl_2\cdot CH(C_{10}H_9ON_3)_2,$$

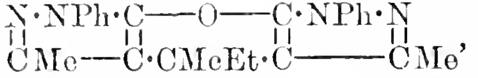
which forms dark yellow crystals, melts at 250°, and when treated with phosphorus oxychloride yields a *product* insoluble in aqueous alkali hydroxides.

Anhydroisopropylidenebis-1-*phenyl*-3-*methylpyrazolone*,



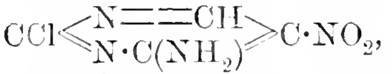
$$\begin{array}{ccccccc}\mathrm{N\cdot NPh\cdot} & \mathrm{C} & \mathrm{{-}O{-}} & \mathrm{C} & \mathrm{\cdot NPh\cdot N}\\ \| & \| & & \| & \quad\|\\ \mathrm{CMe{-}{-}} & \mathrm{C} & \mathrm{\cdot CMe_2\cdot} & \mathrm{C} & \mathrm{{-}{-}CMe}\end{array}$$

is formed by heating 4-*iso*propylenebis-1-phenylmethylpyrazolone (Knorr, Abstr., 1887, 602) with phosphorus oxychloride in a sealed tube at 125—130°; it forms colourless crystals, melts at 163°, boils with only slight decomposition at 400—405°, and is insoluble in aqueous alkali hydroxides, but dissolves in concentrated sulphuric acid. The *platinichloride*, $C_{23}H_{22}ON_4,H_2PtCl_6$, melts above 300°; the yellow, crystalline *aurichloride*, $C_{23}H_{22}ON_4,HAuCl_4$, melts at 256°; the *methiodide*, $C_{23}H_{22}ON_4,MeI$, crystallises in slender needles and melts at 213°; the *dimethiodide*, $C_{23}H_{22}ON_4,2MeI,2H_2O$, crystallises from hot water in needles and decomposes with formation of the monomethiodide at 150—160°. With bromine in glacial acetic acid solution, the anhydro-base forms a *perbromide*, which crystallises in slender, yellow needles, and when treated with aqueous alkali hydroxides forms the *dibromo*-derivative, $C_{23}H_{20}ON_4Br_2$, crystallising in slender, glistening, colourless needles and melting at 239°. The *dinitro*-derivative, $C_{23}H_{20}ON_4(NO_2)_2$, crystallises in yellow needles and melts at 290°. When heated on the water-bath with phosphorus pentachloride, the anhydro-base yields 4:5-dichloro-1-phenyl-3-methylpyrazole (Michaelis and Pasternack, Abstr., 1899, i, 941).

Butylidenebis-1-phenyl-3-methyl-5-pyrazolone, $C_{24}H_{26}O_2N_4$, is formed by heating phenylmethylpyrazolone with methyl ethyl ketone; it separates from alcohol in colourless crystals, melts at 248°, is readily soluble in alcohol, aqueous alkali hydroxides, or acids, and when heated with phosphorus oxychloride at 125—130° yields the *anhydro-base*,  $\begin{array}{l}\mathrm{N\cdot NPh\cdot C{-}{-}O{-}{-}C\cdot NPh\cdot N}\\ \mathrm{CMe{-}{-}C\cdot CMeEt\cdot C{-}{-}{-}{-}CMe}\end{array}$, which separates from alcohol in colourless crystals, melts at 182°, and is insoluble in aqueous alkali hydroxides.

G. Y.

Synthesis of Purine. Oskar Isay (*Ber.*, 1906, 39, 250—265).—

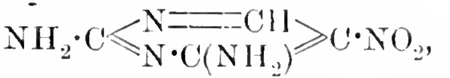
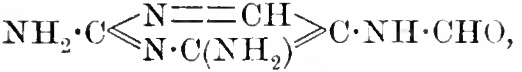
2:4-*Dichloro-5-nitropyrimidine*,  $\mathrm{CCl}{<}\genfrac{}{}{0pt}{}{\mathrm{N{:}CH}}{\mathrm{N\cdot CCl}}{>}\mathrm{C\cdot NO_2}$, prepared by heating 5-nitrouracil with phosphorus oxychloride containing a little hydrochloric acid for about twenty minutes at 185°, crystallises from alcohol, ether, or light petroleum in lustrous leaflets, melts at 29·3°, and boils at 153—155° under 58 mm. pressure. By cold alcoholic ammonia, it is converted into 2-*chloro-5-nitro-4-aminopyrimidine*,  $\mathrm{CCl}{<}\genfrac{}{}{0pt}{}{\mathrm{N{=}{=}CH}}{\mathrm{N\cdot C(NH_2)}}{>}\mathrm{C\cdot NO_2}$, which crystallises from water in white, silky, four-sided prisms, darkens at 205°, decomposes at 217°, and is reduced by hydriodic acid and phosphonium iodide to 4:5-*diaminopyrimidine*,  $\mathrm{CH}{<}\genfrac{}{}{0pt}{}{\mathrm{N{=}{=}CH}}{\mathrm{N\cdot C(NH_2)}}{>}\mathrm{C\cdot NH_2}$; this crystallises from water in aggregates of slender needles, melts at 202·5°, boils at 229° under 32 mm. pressure, and gives the following crystalline salts: the *hydrochloride, hydrobromide, aurichloride, platinichloride*, $2C_4H_6N_4,H_2PtCl_6$; the *picrate* decomposes at 264°. On heating 4:5-diaminopyrimidine with anhydrous formic acid, the *formyl* derivative,

$$\mathrm{CH}{<}\genfrac{}{}{0pt}{}{\mathrm{N{=}{=}CH}}{\mathrm{N\cdot C(NH_2)}}{>}\mathrm{C\cdot NH\cdot CHO},$$

is obtained; it crystallises from alcohol in white leaflets, melts at 198°, and at a higher temperature loses water, giving purine. The latter substance can be prepared directly from 4:5-diaminopyrimidine by heating it with anhydrous formic acid, evaporating the excess of the latter, and subliming the product under reduced pressure.

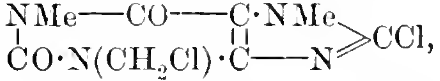
8-*Methylpurine*,  $\begin{array}{l}\mathrm{N{:}CH\cdot C\cdot NH}\\ \mathrm{CH{:}N\cdot C{-}{-}N}\end{array}{>}\mathrm{CMe}$, prepared by heating 4:5-diaminopyrimidine with acetic anhydride at 210° and distilling the product, solidifies in stellar aggregates of needles and melts at 265—266°; the *hydrochloride, hydriodide,* and *platinichloride*, $C_6H_6N_4,H_2PtCl_6$, are crystalline.

On heating 4:5-diaminopyrimidine with carbamide at 165°, it is converted into 8-oxypurine (Fischer and Ach, Abstr., 1898, i, 47). Substituting thiocarbamide for carbamide, 8-*thiopurine*, $C_5H_4N_4S$, is obtained; this crystallises from alcohol in lanceolate needles and begins to decompose at 268°. On melting 4:5-diaminopyrimidine with benzil at 175°, the *azine*,  $\begin{array}{l}\mathrm{N{\cdot}CH{\cdot}C{\cdot}N{:}CPh}\\ \mid \qquad\quad \| \qquad\quad \mid\\ \mathrm{CH{:}N{\cdot}C{\cdot}N{:}CPh}\end{array}$, is formed; it crystallises from alcohol in small, yellow plates and melts at 170·5°.

5-*Nitro-2:4-diaminopyrimidine*,  $\mathrm{NH_2{\cdot}C}\left<\begin{array}{l}\mathrm{N{=\!=}CH}\\ \mathrm{N{\cdot}C(NH_2)}\end{array}\right>\mathrm{C{\cdot}NO_2}$, prepared by heating 2:4-dichloro-5-nitropyrimidine with alcoholic ammonia for two hours at 100°, crystallises from water, in which it is very slightly soluble, in white, rhombic prisms and does not melt at 260°; the *hydrochloride*, *platinichloride*, *aurichloride*, and *picrate* are crystalline; the *sulphate* melts at 201° and the *nitrate* at 213°. On reducing the base with stannous chloride and hydrochloric acid, 2:4:5-*triaminopyrimidine* is obtained; it forms slender needles, may be distilled under reduced pressure, sinters at 176°, and melts at 179°; the *hydrochloride*, *platinichloride*, *sulphate*, and *nitrate* are crystalline, and the *picrate*, $C_4H_7N_5,C_6H_3O_7N_3$, decomposes at 264°. On heating 2:4:5-triaminopyrimidine with formic acid, the *formyl* derivative,  $\mathrm{NH_2{\cdot}C}\left<\begin{array}{l}\mathrm{N{=\!=}CH}\\ \mathrm{N{\cdot}C(NH_2)}\end{array}\right>\mathrm{C{\cdot}NH{\cdot}CHO}$, is produced; it gives well-defined salts, melts at 224°, and at a higher temperature is converted by loss of water into 2-aminopurine or *iso*adenine, which appears to be identical with the substance described by Tafel and Ach (Abstr., 1901, i, 426). 2-Aminopurine does not give the adenine reaction of Kossel and Fischer.

W. A. D.

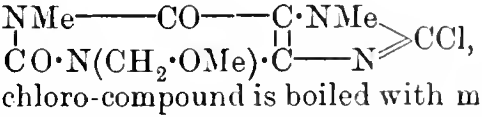
Conversion of Caffeine into Paraxanthine, Theophylline, and Xanthine. EMIL FISCHER and FRIEDRICH ACH (*Ber.*, 1906, 39, 423—435. Compare Abstr., 1896, i, 13).—A 30 per cent. yield of 8-*chloro-3-chloromethylparaxanthine* (3′:8-*dichlorocaffeine*),

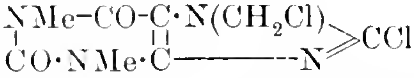


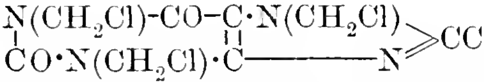
$$\begin{array}{l}\mathrm{NMe{-\!-}CO{-\!-}C{\cdot}NMe}\\ \mid \qquad\qquad\qquad\quad \|\\ \mathrm{CO{\cdot}N(CH_2Cl){\cdot}C{-\!-}N}\end{array}\!\!>\mathrm{CCl},$$

is formed when caffeine, or, better, 8-chlorocaffeine, is heated for eleven hours with a mixture of phosphorus oxychloride and pentachloride at 158—162°. A small amount of a trichlorocaffeine is formed at the same time. An 18 per cent. yield of the dichloro-compound is obtained when chlorine is led into the fused and well-stirred 8-chloro-derivative, first at 200° and then at 170°. It crystallises from a mixture of benzene and ether in nodular aggregates of needles melting at 145—146° (corr.), is readily soluble in cold chloroform, benzene, acetone, or ethyl acetate and in hot ether or alcohol, and gives the murexide reaction with chlorine water.

When boiled with water, the dichloro-derivative is decomposed, and formaldehyde, hydrogen chloride and chloroparaxanthine (Abstr., 1899, i, 173) are formed.

8-*Chloro-3′-methoxycaffeine*,  $\begin{array}{l}\mathrm{NMe{-\!-}CO{-\!-}C{\cdot}NMe}\\ \mid \qquad\qquad\qquad\qquad \|\\ \mathrm{CO{\cdot}N(CH_2{\cdot}OMe){\cdot}C{-\!-}N}\end{array}\!\!>\mathrm{CCl}$, is readily formed when the crude dichloro-compound is boiled with methyl alcohol. It crystallises in colourless, glistening needles, sinters at 126°, and melts at 130—131° (corr.), is very sparingly soluble in ether or hot water, and when heated with fuming hydrochloric acid at 100° yields chloroparaxanthine.

7′ : 8-*Dichlorocaffeine*,  $\begin{array}{l}\text{NMe-CO-C}\cdot\text{N(CH}_2\text{Cl)} \\ \text{CO}\cdot\text{NMe}\cdot\text{C}\text{------N}\end{array}\!\!>\text{CCl}$, is produced by the action of chlorine on a nitrobenzene or phosphorus oxychloride solution of chlorocaffeine at 90—100°. It crystallises from hot methyl alcohol in slender, colourless needles, melts at 150·5—152·5°, is readily soluble in glacial acetic acid or benzene, only sparingly so in hot alcohol, and dissolves in only 70 parts of boiling water. When boiled with ten times its weight of water, it yields 8-chlorotheophylline (Abstr., 1896, i, 263), and with an ethyl-alcoholic solution of sodium ethoxide, 7′ : 8-*diethoxycaffeine*, $C_{12}H_{18}O_4N_4$. This crystallises in colourless, felted needles and melts at 125—126° (corr.). One gram dissolves in about 70 c.c. of warm ether, 10 c.c. of hot alcohol, 90 c.c. of boiling water, or 1250 c.c. of water at 23°.

Tetrachlorocaffeine,  $\begin{array}{l}\text{N(CH}_2\text{Cl)-CO-C}\cdot\text{N(CH}_2\text{Cl)} \\ \text{CO}\cdot\text{N(CH}_2\text{Cl)}\cdot\text{C}\text{------N}\end{array}\!\!>\text{CCl}$, is formed when 7′ : 8-dichlorocaffeine is heated with a phosphorus oxychloride solution of chlorine at 160—162°. It crystallises from ether, melts at 129—130·5° (corr.), and dissolves readily in acetone, acetic acid, or benzene. When boiled with sodium methoxide in methyl-alcoholic solution, it yields *tetramethoxycaffeine*, $C_{12}H_{18}O_6N_4$, which melts at 119—121° (corr.) and dissolves only sparingly in cold ether or water. When boiled with dilute acetic acid, the methoxy-derivative yields chloroxanthine, and this, when reduced with hydriodic acid and phosphonium iodide, gives xanthine. J. J. S.

Condensation of Phenylhydrazine with Ethyl 4-Chloro-3-nitrobenzoate.

ALFRED WERNER and W. PETERS (*Ber.*, 1906, **39**, 185—192).—*Ethyl 2-nitrohydrazobenzene-4-carboxylate*,

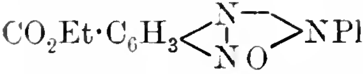
$$CO_2Et\cdot C_6H_3(NO_2)\cdot NH\cdot NHPh,$$

is obtained together with phenylhydrazine hydrochloride when ethyl 4-chloro-3-nitrobenzoate is heated on the water-bath with pure colourless phenylhydrazine (2 mols.). It crystallises from alcohol, melts at 129°, and dissolves readily in alcohol, ether, or acetone.

When the alcoholic solution is oxidised with yellow mercuric oxide, it yields *ethyl* p-*benzeneazo*-m-*nitrobenzoate*,

$$CO_2Et\cdot C_6H_3(NO_2)\cdot N_2\cdot Ph,$$

which crystallises in brilliant red needles melting at 139°. p-*Benzeneazo*-m-*nitrobenzoic acid* is obtained when the ester is hydrolysed with alcoholic potash. It crystallises from alcohol in red needles, melts at 215°, and dissolves in ether, alcohol, or benzene.

When ethyl 4-chloro-3-nitrobenzoate is heated at 90° with commercial phenylhydrazine, the product is *ethyl phenylaznitrosobenzenecarboxylate*,  $CO_2Et\cdot C_6H_3\!<\!\begin{array}{c}\text{N}- \\ | \\ \text{N O}\end{array}\!>\!\text{NPh}$, which crystallises in long, colourless needles melting at 105° and soluble in ether, alcohol, benzene, or acetic acid. The corresponding *acid*, $C_{13}H_9O_3N_3$, crystallises from dilute alcohol in colourless, glistening needles melting at 250° and is insoluble in water. The *potassium* salt, $C_{13}H_8O_3N_3K$, crystallises from alcohol in slender needles. The *hydrazide* of the acid,

$$NH_2\cdot NH\cdot CO\cdot C_6H_3\colon N_3OPh,$$

obtained by the action of hydrazine hydrate on the ester, forms a gelatinous, flocculent mass melting at 220°. The *azoimide*,

$$N_3\cdot CO\cdot C_6H_3\cdot N_3O\cdot Ph,$$

obtained by the action of nitrous acid on the hydrazide, crystallises from benzene in slender, yellow needles melting at 140°.

Phenylaznitrosobenzeneurethane, $CO_2Et\cdot NH\cdot C_6H_3\colon N_3O\cdot Ph$, obtained by boiling the azoimide with absolute alcohol for five to six hours, crystallises in pale yellow needles and melts at 215°. When boiled with alcoholic sodium hydroxide, the urethane compound is hydrolysed to *aminophenylaznitrosobenzene*, $NH_2\cdot C_6H_3\colon N_3O\cdot Ph$, which crystallises from alcohol in greenish-yellow needles melting at 180° and readily soluble in organic solvents and also in hot water. The *hydrochloride* dissolves fairly readily in water. The *acetyl* derivative,

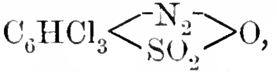
$$NHAc\cdot C_6H_3\colon N_3O\cdot Ph,$$

forms glistening needles and melts at 233°.

Ethyl phenylazimidobenzenecarboxylate, $CO_2Et\cdot C_6H_3\colon N_3\cdot Ph$, obtained by reducing ethyl phenylaznitrosobenzenecarboxylate with stannous chloride and hydrochloric acid, crystallises from alcohol in glistening needles melting at 84° and readily soluble in organic solvents. The corresponding *acid*, $C_{13}H_9O_2N_3$, sublimes in needles, melts at 232°, and dissolves readily in ether, alcohol, or acetic acid. J. J. S.

Substitution of Negative Groups by the Hydroxyl Group in Ortho-substituted Diazonium Salts. EMILIO NOELTING and MARTIN BATTEGAY (*Ber.*, 1906, **39**, 79—86).—2 : 5 : 6-*Trichloroaniline-3-sulphonic acid*, formed by nitration and reduction of 2 : 4 : 5-trichlorobenzene-3-sulphonic acid, crystallises in white needles and is easily soluble in hot, but only sparingly so in cold, water. The *sodium*, $C_6H_3O_3NCl_3SNa,H_2O$, and *barium* salts were analysed.

2 : 5 : 6-*Trichlorobenzenediazonium-3-sulphonic anhydride*,



$$C_6HCl_3<\begin{matrix}-N_2-\\SO_2\end{matrix}>O,$$

prepared by treating the sodium salt of the above acid with hydrochloric acid and sodium nitrite at 20—25°, is obtained as a brown, crystalline powder. It detonates when heated, does not give a precipitate with silver nitrate in aqueous solution, dissolves in concentrated sulphuric acid to form a red solution, and loses nitrogen when heated in aqueous or alcoholic solution. When "coupled" with β-naphthol, it forms the *sodium* salt, $SO_3Na\cdot C_6HCl_3\cdot N\colon N\cdot C_{10}H_6\cdot OH$, which crystallises from glacial acetic acid in glistening, orange needles, dissolves in concentrated sulphuric acid to form a carmine solution, and dyes wool orange. When treated with cuprous chloride in hydrochloric acid solution, the diazonium compound yields 2 : 3 : 4 : 5-*tetrachlorobenzenesulphonic acid*, which crystallises in white needles and is readily soluble in water. The *sodium* salt, $C_6HO_3Cl_4SNa,H_2O$, crystallises in sheaves of white needles; the *barium* salt, ($\frac{1}{2}H_2O$), was analysed.

The action of sodium hydrogen carbonate or acetate on trichlorobenzenediazoniumsulphonic anhydride leads to the formation of *sodium dichlorodiazophenolsulphonate*, which, when treated with cuprous chloride in hydrochloric acid solution, yields *trichlorophenolsulphonic acid*. This crystallises in slender, white needles; the *sodium* salt, $C_6H_2O_4Cl_3SNa,1\frac{1}{2}H_2O$, forms white needles; the *barium* salt is only sparingly soluble.

When "coupled" with β-naphthol in alkaline solution, sodium dichlorodiazophenolsulphonate forms a violet *disodium* salt, which on treatment with dilute hydrochloric acid yields the *monosodium* salt, $OH\cdot C_6HCl_2(SO_3Na)\cdot N{:}N\cdot C_{10}H_6\cdot OH$; this crystallises in glistening, brown needles, dissolves in water to form a violet solution, gives a violet coloration with alkali hydroxides or concentrated sulphuric acid, and on reduction yields 3 : 6-dichloro-2-aminophenol-4-sulphonic acid (Julius, *Chem. Zeit.*, 1903, **27**, 846). The azo-compound dyes wool brownish-red, becoming violet-brown when treated with an alkali hydroxide; on treatment with potassium dichromate and sulphuric acid, there is obtained a violet colour, fast to alkali hydroxides. When treated with copper sulphate, the dyed wool becomes carmine-red.

The *azo-dye*, $SO_3Na\cdot C_6HBr_3\cdot N{:}N\cdot C_{10}H_6\cdot OH$, obtained by "coupling" diazotised 2 : 4 : 6-tribromoaniline-3-sulphonic acid with β-naphthol in alkaline solution, forms a carmine-red solution in concentrated sulphuric acid, dyes shades which are stable towards alkali hydroxides, and when treated with sodium hydrogen carbonate yields a *product* in which a bromine atom is substituted by a hydroxyl group. When "coupled" with β-naphthol, this forms the *azo-dye*,

$$OH\cdot C_6HBr_2(SO_3Na)\cdot N{:}N\cdot C_{10}H_6\cdot OH,$$

which crystallises in glistening, brown needles, dissolves in water to form a violet-red, in aqueous alkali hydroxides to form a violet, solution containing the *disodium* salt, and gives a bluish-violet coloration with concentrated sulphuric acid. It dyes wool a red shade, which changes to dark violet, and becomes fast to alkali hydroxides when treated with chromic acid.

When "coupled" with β-naphthol, the diazonium anhydride obtained from 2 : 5-dichloroaniline-4-sulphonic acid (Noelting and Kopp, Abstr., 1905, i, 873) forms the *azo-dye*, $SO_3Na\cdot C_6H_2Cl_2\cdot N{:}N\cdot C_{10}H_6\cdot OH$, which crystallises in red needles and in its properties resembles Orange II. When treated with sodium hydrogen carbonate, the diazonium anhydride is converted into the corresponding *o*-hydroxy-compound only to the extent of 40 per cent.; when coupled with β-naphthol, the resulting mixture of diazo-compounds yields a red *product* which has the properties of an *o*-hydroxyazo-compound.

o-*Chloroaniline*-p-*sulphonic acid* is formed by heating *o*-chloroaniline hydrogen sulphate at 160° under 20—30 mm. pressure. The *sodium* salt, ($4H_2O$), crystallises in needles and is only sparingly soluble in water. When treated with bromine, it forms 2-chloro-4 : 6-dibromaniline, melting at 103° (m. p. 93·5°; Fittig and Buchner, Abstr., 1878, 50). When diazotised and "coupled" with β-naphthol, *o*-chloroaniline-*p* sulphonic acid yields an *azo-dye* resembling Orange II. The action of sodium hydrogen carbonate on the diazonium anhydride leads to substitution of only 25 per cent. of the chlorine by hydroxyl; on "coupling" the resulting mixture, a *product* is obtained which dyes dirty-yellow shades, is only slightly altered by treatment with chromic acid, and does not exhibit the properties of an *o*-aminophenol derivative.

The β-naphthol *dye*, $SO_3Na\cdot C_6H_3(NO_2)\cdot N\colon N\cdot C_{10}H_6\cdot OH,H_2O$, obtained from the diazonium anhydride of *o*-nitraniline-*p*-sulphonic acid (Nietzki and Lerch, Abstr., 1889, 144), crystallises in red needles, dyes wool a redder tone than does Orange II, and is stable towards alkali hydroxides. The diazonium anhydride dissolves in aqueous sodium hydrogen carbonate below 40°, with evolution of carbon dioxide and formation of *sodium diazophenolsulphonate*. The solution "couples" with β-naphthol in presence of sodium hydroxide to form the *azo-dye*,

$$OH\cdot C_6H_3(SO_3Na)\cdot N\colon N\cdot C_{10}H_6\cdot OH,$$

which crystallises in glistening, black needles and dissolves in concentrated sulphuric acid to a bluish-violet solution. G. Y.

Diazo-derivatives of Diamines (Phenylenediamines, Benzidine). Léo Vignon (*Compt. rend.*, 1906, **142**, 159—161).—A solution of diazobenzene chloride is decomposed by *o*- or *p*-phenylenediamine, and with *m*-phenylenediamine yields chrysoidine. Diazotised benzidine combines readily with amines and phenols to form stable derivatives.

The author attributes this difference in the behaviour of the two types of diamines to the fact that in the former the two amino-groups are attached to the same benzene nucleus and either cannot be diazotised, as in the case of the ortho-compound, or yield very unstable diazo-compounds, as in the case of the meta- and para-compounds; whilst in the latter, the two amino-groups, being attached to different benzene nuclei, are diazotised as readily as the monoamines.

M. A. W.

The Combination of more than One Molecule of a Diazo- or Tetrazo-compound in the production of Azo-dyes. Wilhelm Vaubel and Otto Scheuer (*Zeit. Farb.-Ind.*, 1906, **5**, 1—2).—In the preparation of benzidine-blue from tetrazodiphenyl and R-salt, an excess of tetrazodiphenyl converts the dye into a substance insoluble in water and aqueous alkalis. The product seems to contain tetrazodiphenyl and R-salt in the ratio $3C_{12}H_8N_4\colon OH\cdot C_{10}H_5(SO_3Na)_2$; the original sulphonic groups appear to be present, but diazo- or diazoxy-groups cannot be detected. W. A. D.

Properties of Columbin, an Albumin from the White of Pigeons' Eggs. Alexei A. Panormoff (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 915—923. Compare Abstr., 1900, i, 709).—In addition to columbinin (*loc. cit.*), the author has separated from the white of pigeons' eggs another albumin, *columbin*, which has the composition: C, 52·47; H, 7·16; N, 14·82 per cent. These two albumins occur in equal proportions in the white of pigeons' eggs. Columbin is unstable and gives acid aqueous solutions, from which it is precipitated by alcohol, a solution of mercuric iodide in potassium iodide, or ammoniacal lead acetate solution. It has $[\alpha]_D$ −36·33° at 20°. *Columbin hydrochloride* has $[\alpha]_D$ −67·21° in aqueous solution, or −87·27° after being heated at 100° for some time; on analysis, it gives the following numbers: C, 50·67; H, 6·87; N, 14·03; Cl, 2·85; S, 1·34 per cent.

The *hydrobromide* has $[\alpha]_D$ −87·39° after heating in solution at 100°; its composition was determined. T. H. P.

Properties of Albumins found in the White of Ducks' Eggs.

Alexei A. Panormoff (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 923—930).—The white of ducks' eggs contains only two albumins, to which the names *anatinin* and *anatin* are given; these occur in the proportion of two parts of the former to one of the latter.

Anatin is precipitable by dilute ammonium sulphate solution, has $[\alpha]_D$ −81·95° at 20°, and yields the following numbers on analysis: C, 50·32; H, 6·84; N, 14·64; S, 2·96. The hydrochloride has $[\alpha]_D$ −77·2° at 20° in freshly-prepared solutions or −80·71° in solutions previously heated at 100°.

Anatinin is precipitated by concentrated ammonium sulphate solution, has $[\alpha]_D$ −37·09° at 20°, and has the composition: C, 52·15; H, 7·30; N, 14·92; S, 2·01 per cent. Its hydrochloride has $[\alpha]_D$ −39·22° at 20°. T. H. P.

Albumin from the Blood-serum of the Cow.

Stephan Maximowitsch (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 931—940).—By fractional precipitation of serum from defibrinated cows' blood with ammonium sulphate, the author has obtained an albumin which has the formula $C_{357}H_{552}O_{123}N_{93}S_3$ and $[\alpha]_D$ −48·36° at 20°, and resembles the albumin separated from the serum of horses' blood (Abstr., 1902, i, 66). The *hydrochloride*, Alb., 7HCl, has $[\alpha]_D$ −77·75° at 20° in freshly-prepared solutions and −84·05° after heating at 100°. The *phosphate*, Alb., $3H_3PO_4$, has $[\alpha]_D$ −71·38° at 20° or −82·52° after heating at 100°. T. H. P.

Precipitation of Serum-globulin from Blood-serum by means of Acetic Acid.

Willem Huiskamp (*Zeit. physiol. Chem.*, 1905, **46**, 394—400).—The proteid precipitated by the addition of dilute acetic acid to diluted serum appears to be the same substance as that obtained by Hammarsten as a precipitate when 0·3 per cent. of sodium chloride is added. The reactions and elementary composition of the two are identical. It is further identical with serum-globulin. It is precipitated almost entirely by one-third saturation with ammonium sulphate and therefore consists chiefly of euglobulin. W. D. H.

Animal Gelatins. IV.

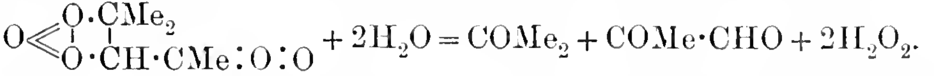
Wl. S. Sadikoff (*Zeit. physiol. Chem.*, 1905, **46**, 387—393. Compare Abstr., 1904, i, 462).—Gelatins or glutins differ in many of their solubilities from gluteins or cartilage-glutins. By means of saline solutions, gelatin is divisible into (1) a part which is insoluble in salt solution, (2) a part soluble in salt solution but precipitated by acid, and (3) a part soluble in both salt solution and acids. W. D. H.

Organic Chemistry.

Preparation of Methane. Herbert S. Elworthy and Ernest H. Williamson (D.R.-P. 161666).—A gas, consisting principally of methane, may be prepared by passing a mixture of carbon monoxide (1 vol.) and hydrogen (3 vols.) over finely-divided nickel at 250°. The mixture is obtained by adding the necessary quantity of hydrogen, preferably prepared by the action of steam on heated iron, to water-gas which has been freed from carbon dioxide. A suitable apparatus is described and illustrated. C. H. D.

Action of Ozone on Organic Compounds. Carl D. Harries (*Annalen*, 1905, **343**, 311—375).—A *résumé* of the earlier work on the action of ozone on the organic compounds is given. Hydrocarbons, such as methane and ethylene, are attacked and also alcohols, in which case aldehydes, acids, and hydrogen peroxide are formed. Occasionally explosive peroxides of unknown constitution have been obtained.

In a long series of papers (Abstr., 1903, i, 605; 1904, i, 413; 1905, i, 15, 361, 757, 861) it has been shown that unsaturated hydrocarbons and unsaturated alcohols combine with one molecule of ozone to form ozonides, whilst unsaturated ketones, aldehydes, and monobasic acids combine with four atoms of oxygen, one molecule of ozone combining at the ethylene linking, and the fourth atom of oxygen with the carbonyl group. The constitution of the ozonides is demonstrated by their reaction with water, thus: the ozonide of mesityl oxide yields, with water, acetone, pyruvic aldehyde, and hydrogen peroxide:



$$O\Big\langle\begin{matrix}O\cdot CMe_2\\ | \qquad | \\ O\cdot CH\cdot CMe:O:O\end{matrix} + 2H_2O = COMe_2 + COMe\cdot CHO + 2H_2O_2.$$

Methylheptenone yields with ozone an ozonide which decomposes immediately into an acetone peroxide and an aldehyde:

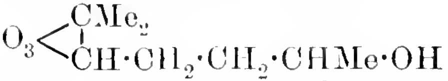
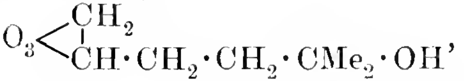
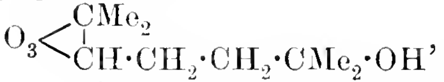
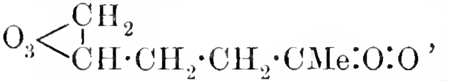
$$O\Big\langle\begin{matrix}O\cdot CMeR\\ | \qquad | \\ O\cdot CHR\end{matrix} \longrightarrow R\cdot CMe\Big\langle\begin{matrix}O\\ | \\ O\end{matrix} + R\cdot CHO,$$

no hydrogen peroxide being formed. On the other hand, mesityl oxide and methylheptenoneozonide both yield with water hydrogen peroxide. It follows, therefore, that the hydrogen peroxide arises from the oxygen atom linked to the carbonyl group. It should be noted that the group $R\cdot CMe:C<$ always yields with ozone an acetone peroxide.

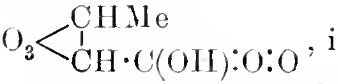
Generally it can be said that ozone acts on organic compounds in two ways: (1) forming an ozonide, when the ozone attaches itself to an unsaturated carbon linking, and (2) when the ozone molecule is decomposed, labile peroxides of the carbonyl group being formed.

The formation of triozonides of benzene is in favour of the Kekulé formula of benzene, but opposed to the centric formula. Similarly, diphenyl yields a *tetraozonide*, facts which indicate the presence of ethylene linkings resembling those of the aliphatic series. Naphthalene yields a *diozonide* only, from which it can be concluded that the linkings in the two naphthalene nuclei are different. It appears, in consequence, that a centric structure is inactive to ozone.

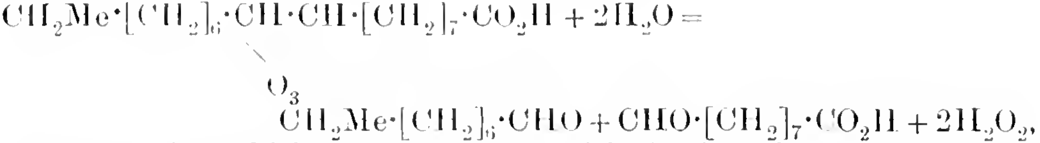
[With Kurt Langheld.]—The ozonides were prepared by passing ozone through the dried substance, a process which must be carried on for about two hours for each three grams of ozonide produced; the ozonide is purified by dissolving it in ethyl acetate and precipitating by light petroleum.

The *ozonide* of allyl alcohol,  $O_3<\begin{array}{l}CH_2\\|\\CH\cdot CH_2\cdot OH\end{array}$, is a syrup decomposing at the ordinary temperature and yielding an aldehyde when boiled with water; when distilled under reduced pressure, it decomposes in a similar manner. The *ozonide* of secondary methylheptenol,  $O_3<\begin{array}{l}CMe_2\\|\\CH\cdot CH_2\cdot CH_2\cdot CHMe\cdot OH\end{array}$, is an oil having a sp. gr. 1·0992 at 25·5°. Tertiary methylhexenol is prepared from allylacetone and magnesium methiodide, and is a liquid boiling at 57° under 16 mm. pressure. The *ozonide*,  $O_3<\begin{array}{l}CH_2\\|\\CH\cdot CH_2\cdot CH_2\cdot CMe_2\cdot OH\end{array}$, is a liquid having a sp. gr. 1·0703 at 23·5°. The *ozonide* of tertiary dimethylheptenol,  $O_3<\begin{array}{l}CMe_2\\|\\CH\cdot CH_2\cdot CH_2\cdot CMe_2\cdot OH\end{array}$, has a sp. gr. 1·0603 at 23·5°, and is decomposed by water into acetone and an aldehyde. The *ozonide* of allylacetone,  $O_3<\begin{array}{l}CH_2\\|\\CH\cdot CH_2\cdot CH_2\cdot CMe{:}O{:}O\end{array}$, is an explosive syrup with a sp. gr. 1·1814 at 19°, and is decomposed by boiling with water into formaldehyde, lævulinaldehyde, and hydrogen peroxide.

The treatment of methylheptenone with ozone leads to the formation of acetone peroxide. If the crude product of ozonisation is boiled with water, lævulinaldehyde is produced together with acetone peroxide.

The *ozonide* of citronellal, $C_{10}H_{18}O_5$, is a syrup having a sp. gr. 1·0746 at 21°; it decomposes on distillation into the aldehyde and oxygen, and appears when boiled with water to form a ketonealdehyde. The *ozonide* of citral, $C_{10}H_{16}O_5$, is a syrup having a sp. gr. 1·1486 at 21°, and is decomposed by warming with water. The two ozonides last mentioned possess molecular weights differing considerably from the unimolecular formulæ. The *ozonide* of *iso*crotonic acid,  $O_3<\begin{array}{l}CHMe\\|\\CH\cdot C(OH){:}O{:}O\end{array}$, is an extremely explosive syrup, which decomposes into oxygen and *iso*crotonic acid when kept. If a solution of *iso*crotonic acid in water is ozonised, acetaldehyde and glyoxylic acid are formed; hence, the constitution of the ozonide is determined. *Œnanthyl peroxide*, $CH_2Me\cdot[CH_2]_4\cdot CH{:}O{:}O$, prepared from œnanthaldehyde is an oil having a sp. gr. 0·9081 and $n_D = 1·42876$ at 8°. It is decomposed by water into the aldehyde and hydrogen peroxide; it decomposes with development of heat into heptoic acid, a change which is accelerated by the presence of alkali; dilute acids bring about the evolution of oxygen.

[With Carl Thieme.]—Treatment with ozone has been used to ascertain the relation of the isomerides, oleic and elaidic acids. The ozonides of both acids are decomposed by water according to the equation :



$$\mathrm{CH_2Me\cdot[CH_2]_6\cdot\underset{\diagdown\, O_3}{CH\cdot CH}\cdot[CH_2]_7\cdot CO_2H + 2H_2O = CH_2Me\cdot[CH_2]_6\cdot CHO + CHO\cdot[CH_2]_7\cdot CO_2H + 2H_2O_2},$$

an observation which is in agreement with the fact that both dibromooleic and dibromoelaidic acids yield the same stearolic acid. A solution of sodium oleate was ozonised and then evaporated under reduced pressure ; nonylaldehyde and pelargonic acid, $C_8H_{17}\cdot CO_2H$, are extracted from the distillate by ether, and can be separated by distillation under a pressure of 15 mm. The residual alkaline liquor was acidified and extracted with ether, giving azelaic acid (m. p. 106°). The *semicarbazone* of nonylaldehyde, $C_9H_{18}\colon N\cdot NH\cdot CO\cdot NH_2$, crystallises in leaflets melting at 84°.

The ozonisation of elaidic acid could only be carried out in chloroform solution ; the *ozonide* is a gelatinous mass which, when heated with water, gives hydrogen peroxide ; it reduces Fehling's solution, oxidises potassium iodide, and decolorises indigo and potassium permanganate. The *ozonide* of oleic acid prepared in the same way has similar properties. The *calcium* salt of pelargonic acid is a powder melting at 216° ; the *silver* salt is sensitive to light. The half aldehyde of azelaic acid has been isolated in the form of the *semicarbazone*, $NH_2\cdot CO\cdot NH\cdot N\colon CH\cdot[CH_2]_7\cdot CO_2H$, from the acidified alkaline liquor obtained in the ozonisation of sodium oleate ; it melts at 163°.

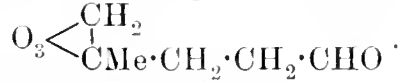
[With HANS TÜRK.]—The constitution of several hydrocarbons has been elucidated by their reaction with ozone. Diallyl has been shown to have the constitution represented by the formula

$$CH_2\colon CH\cdot CH_2\cdot CH_2\cdot CH\colon CH_2 ;$$

it is converted into a *diozonide*, $C_6H_{10}O_6$, by treatment with ozone in chloroform solution ; the diozonide is an explosive syrup, which reacts with water giving a mixture of succinic acid and succinaldehyde. The hydrocarbon, C_9H_{16}, prepared by Harries and Weil (Abstr., 1904, i, 361), has been shown to be $\beta\zeta$-dimethyl-$\Delta^{\beta\zeta}$-heptadiene,

$$CMe_2\colon CH\cdot CH_2\cdot CH_2\cdot CMe\colon CH_2,$$

and not the $\Delta^{\beta\epsilon}$-heptadiene ; it was previously stated that its diozonide did not give lævulinaldehyde, but it is now found that the diozonide, $C_9H_{16}O_6$, yields the aldehyde on prolonged boiling with water. If the hydrocarbon is treated with ozone under water, it passes into solution ; both hydrogen peroxide and an aldehyde can be detected in the solution, and on evaporating an explosive syrup is left, having probably the constitution



$$O_3\!<\!\begin{matrix}CH_2\\ |\\ CMe\cdot CH_2\cdot CH_2\cdot CHO\end{matrix}\ .$$

The hydrocarbon, *$\beta\epsilon$-dimethyl-$\Delta^{\beta\epsilon}$-hexadiene*,

$$CH_2\colon CMe\cdot CH_2\cdot CH_2\cdot CMe\colon CH_2,$$

is an oil boiling at 137° under 755 mm. pressure ; on repeated distillation, the boiling point falls to 115—117°. The *dibromide*, prepared by treatment with hydrogen bromide in acetic acid solution, melts at 71°. The hydrocarbon is prepared from *$\beta\epsilon$-dimethylhexane-$\beta\epsilon$-diol*,

$$OH\cdot CMe_2\cdot CH_2\cdot CH_2\cdot CMe_2\cdot OH,$$

which is obtained from magnesium methyl iodide and ethyl succinate and crystallises in leaflets melting at 89°. It is converted by hydrogen bromide in acetic acid solution into *βε-dimethylhexane-βε-dibromide*, $CBrMe_2\cdot CH_2\cdot CH_2\cdot CBrMe$, which melts at 71° and loses hydrogen bromide when exposed to the air. When boiled with pyridine, it yields a mixture, the main constituent of which is the hydrocarbon just described; at the same time, a solid hydrocarbon, C_8H_{14}, which melts at $-5°$ and boils at 142°, is formed; it is readily oxidised by the air to a compound, $C_8H_{14}O_2$, and combines with hydrogen bromide, yielding an oil, $C_8H_{15}Br$, which combines with bromine and decolorises permanganate. βε-Dimethyl-$\Delta^{\alpha\epsilon}$-hexadiene yields a *diozonide*, $C_8H_{14}O_6$, which is a yellow, explosive liquid and decomposes on keeping, formaldehyde being produced. When the hydrocarbon is treated with ozone in the presence of water, formaldehyde, hydrogen peroxide, and acetonylacetone are produced. These facts are evidence for the constitution of the hydrocarbon.

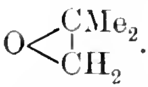
[With VALENTIN WEISS.]—Renard's "ozotoluene," $C_7H_8O_6$ (*Compt. rend.*, 1895, **121**, 651), prepared from toluene and ozone at 0°, appears to have the formula $C_7H_8O_7$ and to be a decomposition product of the triozonide, which is only formed at $-21°$ and decomposes explosively at the ordinary temperature. On boiling the ozotoluene with water, methylglyoxal and glyoxal are formed. m-*Xylenetriozonide* is only formed at very low temperatures. *Mesitylenetriozonide*, $C_6H_3Me_3(O_3)_3$, is a gelatinous material which explodes at the ordinary temperature; it yields with water methylglyoxal, which can be isolated as a *disemicarbazone* (m. p. 255—257°).

Naphthalenediozonide is obtained as explosive crystals by passing ozone into a chloroform solution of naphthalene; when decomposed with water, phthalaldehyde and phthalic acid are formed.

The *diozonide* of phenanthrene, $C_{14}H_{10}O_6$, and the *tetraozonide* of diphenyl are explosive, crystalline substances.

Attempts have been made to prepare Berthelot's ethyl peroxide, Et_4O_3; ozone and carbon dioxide were passed into dry ether, the ether evaporated under reduced pressure, and the residue distilled under 20 mm. pressure at 40—50°. The colourless, viscid liquid deposited crystals at a very low temperature and exploded when air was admitted. The carbon was 15·28—25·65 per cent., and not 58·54 per cent., as Berthelot's formula requires. K. J. P. O.

The Addition of Hydrogen Chloride to *iso*Butylene Oxide,



$O<\begin{matrix}CMe_2\\|\\CH_2\end{matrix}$. LOUIS HENRY (*Compt. rend.*, 1906, **142**, 493—497).—*iso*Butylene oxide, obtained by the action of dry powdered potassium hydroxide on chlorotrimethyl carbinol, $CH_2Cl\cdot CMe_2\cdot OH$ (prepared from magnesium methyl bromide, chloroacetone, and ethyl chloroacetate), combines readily with hydrogen chloride to form *β-chloroisobutyl alcohol*, $CMe_2Cl\cdot CH_2\cdot OH$, which is a thick, colourless liquid with an agreeable odour, boils at 132—133°, and does not solidify in a mixture of solid carbon dioxide and ether, and in this respect differs from its isomeride chlorotrimethylcarbinol (compare Krassusky, Abstr., 1901, i, 246), which forms a crystalline solid melting at $-20°$. When heated with hydrochloric acid at 60°, β-chloro*iso*butyl alcohol forms the ether, $(CMe_2Cl\cdot CH_2)_2O$, dissolves in a mixture of nitric and sulphuric acids to form the nitrate, $CMe_2Cl\cdot CH_2\cdot NO_3$, and reacts with nitrous acid to form the nitrite, $CMe_2Cl\cdot CH_2\cdot O\cdot NO$, whilst chlorotrimethylcarbinol yields *αβ*-dichloro*iso*butane with hydrochloric acid and does not react with a mixture of nitric and sulphuric acids nor with nitrous acid.

M. A. W.

Reactions between Lead Chloride and Lead Acetate in Acetic Acid and Water Solutions. JOHN WHITE (*Amer. Chem. J.*, 1906, **35**, 217—227).—When lead chloride is dissolved in a hot solution of lead acetate in glacial acetic acid, a double *salt*,

$$PbCl(C_2H_3O_2),C_2H_4O_2,$$

is obtained, which forms monoclinic, prismatic crystals and, when left in the air, gradually loses a portion of its acid of crystallisation.

Carius (*Annalen*, 1863, **125**, 87) has shown that lead chloride dissolves in an aqueous solution of lead acetate to form a salt to which he assigned the formula $PbCl(C_2H_3O_2),Pb(C_2H_3O_2)_2,3H_2O$. It is now found that this salt crystallises in tufts of silky needles and has a composition which is represented by one of the formulæ, $PbCl(C_2H_3O_2),Pb(C_2H_3O_2)_2,H_2O$; $PbCl(C_2H_3O_2),Pb(C_2H_3O_2)_2,2H_2O$; or $PbCl(C_2H_3O_2),Pb(C_2H_3O_2)_2,\frac{1}{2}C_2H_4O_2$, between which it was not possible to decide. A determination of the molecular weight of this salt by the cryoscopic method, using water as the solvent, gave a value about one-fourth of that required by any of the proposed formulæ, indicating that dissociation had taken place ; similar results were obtained with the double calcium salt, $CaCl(C_2H_3O_2),5H_2O$, described by Fritsche (*Ann. Phys. Chem.*, 1833, **28**, 121).

The behaviour of lead chloride towards alkali acetates is different from that of lead iodide, the chloride undergoing double decomposition, whilst, as has been shown previously (Abstr., 1904, i, 134), the iodide combines with them to form double salts. E. G.

Reactions involved in the Formation of certain Complex Salts of Lead. JOHN WHITE and J. M. NELSON (*Amer. Chem. J.*, 1906, **35**, 227—235).—Experiments have been made with the object of preparing the salt $PbI\cdot C_2H_3O_2$, but without success. When lead acetate is heated with methyl iodide and a mixture of acetic acid and acetic anhydride, the double *salt*, $5PbI\cdot C_2H_3O_2,Pb(C_2H_3O_2)_2$, is obtained, which forms monoclinic crystals. It has been found that in order to prevent the formation of lead iodide in the preparation of this salt, the temperature should not be allowed to exceed 70—75°, and that certain conditions of concentration and relative proportions of the reacting substances must be observed. The results of the experiments indicate that the salt $PbI\cdot C_2H_3O_2$ is formed as an intermediate compound. E. G.

Nitration in the Presence of Phosphoric Oxide. ROBERT BEHREND and HANS OSTEN (*Annalen*, 1905, **343**, 152—155).—A mixture of fuming nitric acid and phosphoric oxide has been tried as a nitrating mixture ; generally it is not to be preferred to the ordinary methods. Ethyl acetoacetate yields the peroxide of ethyl di*iso*nitrososuccinate. Similarly, nitrotartaric acid and tartronic acid can be easily prepared when tartaric acid is treated with a mixture of nitric acid and the phosphoric oxide; the first-mentioned acid is produced immediately, whilst the tartronic acid is formed when the mixture is kept for two weeks. Nitrohydantoin can be easily prepared from hydantoin. K. J. P. O.

Synthesis of Derivatives of Ethyl Acetoacetate. II. MILORAD Z. JOVITSCHITSCH (*Ber.*, 1906, **39**, 784—788. Compare Abstr., 1902, i, 202).—The action of nitric acid (1 mol.) of sp. gr. 1·15 on ethyl *iso*nitrosoacetoacetate leads to the formation of the nitrolic acid of ethyl acetate, which, when shaken with an excess of hydrochloric acid of sp. gr. 1·2, yields ethyl chloro-oximinoacetate. The nitrolic acid and the chloro-oximinoacetate are obtained in almost quantitative yields. The action of chlorine on the nitrolic acid of ethyl acetate in aqueous or ethereal solution leads to the formation of a number of products, amongst which are ethyl chloro-oximinoacetate and the oily peroxide of ethyl di*iso*nitrososuccinate, whilst on further treatment with chlorine, the chloro-oximinoacetate is decomposed.

Ethyl bromo-oximinoacetate, $OH\cdot N\colon CBr\cdot CO_2Et$, formed by the action of bromine on the nitrolic acid or on ethyl chloro-oximinoacetate, crystallises in small, snow-white needles, has a burning taste, melts at 85—86°, and is readily soluble in ether or benzene, but only sparingly so in light petroleum or water. It interacts with aniline, forming ethyl *iso*nitrosoanilinoacetate, and yields hydroxylamine when boiled with dilute hydrochloric acid. G. Y.

Dehydration of Hydroxy-β-alkylpivalic Esters. ALFRED P. COURTOT (*Bull. Soc. chim.*, 1906, [iii], **35**, 111—133).—When ethyl hydroxymethylpivalate [ethyl β-hydroxy-*αα*-dimethylbutyrate] is prepared by Bouveault's method (Abstr., 1900, i, 131), there is also formed some ethyl hydroxypropenylpivalate, $CHMe\colon CH\cdot CH(OH)\cdot CMe_2\cdot CO_2Et$ (Jaworsky, Abstr., 1903, i, 729), in addition to the diethyl pentamethylglutarate observed by Bouveault (*loc. cit.*).

β-Hydroxy-*αα*-dimethylbutyric acid, $OH\cdot CHMe\cdot CMe_2\cdot CO_2H$, prepared by saponifying the ethyl ester with potassium hydroxide in alcohol, forms a crystalline, hygroscopic mass, melts at 31°, and boils at 148° under 15 mm. pressure. When heated with benzylamine at 180°, no benzylamide is formed; the *benzylamine* salt melts at 71°. The *acetyl* derivative, obtained by the action of acetyl chloride on the acid, separates from light petroleum in large crystals, melts at 58°, and boils at 147° under 12 mm. pressure. The *phenylcarbamate* crystallises from a mixture of ether and light petroleum and melts at 129°. When the acid is heated with excess of hydriodic acid, it is converted into *β-iodo-αα-dimethylbutyric acid*, which crystallises from light petroleum and melts at 44°.

Ethyl β-hydroxy-*αα*-dimethylbutyrate is a viscous liquid and boils at 91° under 13 mm. pressure (compare Bouveault, *loc. cit.*), the *acetyl* derivative is viscous and boils at 110° under 24 mm. pressure. The *phenylcarbamate* crystallises from a mixture of ether and light petroleum in colourless needles and melts at 86°. When the ester, dissolved in benzene, is treated with phosphoric oxide, it undergoes dehydration, furnishing ethyl αα-dimethyl*iso*crotonate, $CH_2{:}CH\cdot CMe_2\cdot CO_2Et$, which boils at 141—142° and on hydrolysis with potassium hydroxide in alcohol furnishes the *acid*. This is a colourless, mobile liquid, which boils at 99° under 23 mm. pressure and at 185° under atmospheric pressure, and has a sp. gr. 0·9567 at 15°. It solidifies when cooled and then melts at −6°. The *zinc*, *copper*, *calcium*, *barium*, and *lithium* salts were prepared. The *chloride* is a liquid of pungent odour, which boils at 26° under 14 mm. pressure. The *phenylhydrazide* crystallises from ether and melts at 98°, the *anilide* separates from a mixture of ether and light petroleum in large crystals and melts at 83°, and the *amide*, obtained by saturating the chloride with dry ammonia, forms small, white crystals, melts at 93°, and is very soluble in ether, alcohol, or water.

When αα-dimethyl*iso*crotonic acid is treated with bromine in chloroform solution, it is converted into *βγ-dibromo-αα-dimethylbutyric acid*, which crystallises from a mixture of ether and light petroleum in groups of slender needles and melts at 90°.

On reduction with sodium, αα-dimethyl*iso*crotonic acid yields the corresponding *dimethylbutenol*, $CH_2{:}CH\cdot CMe_2\cdot CH_2\cdot OH$. This is a mobile, almost odourless liquid boiling at 130—131°. The *acetate* is a liquid of pleasant odour and boils at 149°. The *phenylcarbamate* crystallises from light petroleum in long needles and melts at 68—69°.

αα-Dimethyl*iso*crotonic acid combines with one mol. of hydrogen iodide to form the β-iodo-αα-dimethylbutyric acid described above, and on oxidation with potassium permanganate in presence of potassium hydrogen carbonate yields dimethylmalonic acid. T. A. H.

Simple and Complex Salts of Bismuth. ARTHUR ROSENHEIM and WALTER VOGELSANG (*Zeit. anorg. Chem.*, 1906, **48**, 205—216).—[With M. Koss.]—When bismuth nitrate, dissolved in nitric acid, is treated with three molecular equivalents of tartaric acid, the *compound* $Bi(C_4H_4O_6)NO_3,5H_2O$ separates in colourless, prismatic crystals. On dissolving this salt in a concentrated boiling solution of tartaric acid and allowing to cool, the *compound* $BiH(C_4H_4O_6)_2,2H_2O$ is obtained in lustrous needles. Both compounds are decomposed by water with formation of basic salts. Contrary to the statements of Baudran (Abstr., 1900, i, 375) and others, salts corresponding with antimony potassium tartrate could not be obtained.

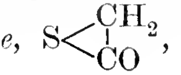
From the solution of the salt last mentioned in excess of alkali, a *compound* of the empirical formula $KBi_3C_4H_{10}O_{13}$, perhaps

$$K(BiO)C_4H_2(BiO)_2O_6,6H_2O,$$

separates in small crystals soluble without decomposition in water; the same compound is also obtained by other methods. Its aqueous solution is strongly dextrorotatory, but with increasing amounts of alkali the rotation diminishes and finally changes sign. From a nitric acid solution of bismuth nitrate to which excess of alkali had been added, a second *compound*, $K_2BiC_4H_3O_7$, was obtained in lustrous scales. From observations of the effect on polarised light of tartaric acid solutions to which varying amounts of bismuth nitrate and sodium hydroxide had been added, the conclusion is drawn that other complex salts besides those of the above type exist. Complex sodium salts have not been obtained in crystalline form, but an ammonium salt, $NH_4BiC_4H_2O_6$, has been isolated in the form of microscopic prisms.

From a solution of thiocyanic acid saturated with bismuth carbonate, the *compound* $Bi(SCN)_2\cdot OH,5H_2O$ separates in glistening plates on addition of alcohol. When excess of the acid is added and the solution concentrated, normal *bismuth thiocyanate*, $Bi(SCN)_3,14H_2O$, is obtained in deep red, transparent needles. When potassium thiocyanate is added to the same solution, the *compound* $K_3Bi(SCN)_6$, already described by Vanino and Hauser (Abstr., 1902, i, 14), separates. On the other hand, the *compound* $K_9Bi(SCN)_{12}$, described by these authors, could not be obtained and probably does not exist.

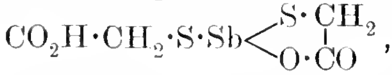
Normal *bismuth acetate*, $Bi(C_2H_3O_2)_3$, recently described by Colonna (Abstr., 1905, i, 852), has been obtained by boiling the carbonate with glacial acetic acid in the presence of mannitol. G. S.

Thioglycollic Acid. PETER KLASON and TOR CARLSON (*Ber.*, 1906, **39**, 732—738).—The yield of thioglycollic acid from the action of potassium hydrosulphide on chloroacetic acid is better the more water is present. When thioglycollic acid is heated under diminished pressure, various condensation products are formed according to the conditions; in one case, a compound crystallising from benzene as a snow-white powder, melting at about 80°, and giving numbers on analysis corresponding with those for *thioglycollide*,  $S<\begin{matrix}CH_2\\ | \\ CO\end{matrix}$, was obtained.

Determinations of the electrical conductivity of thioglycollic acid gave $K = 0{\cdot}0291$, a value at variance with that obtained by Ostwald, who found $K = 0{\cdot}0225$.

Ethyl thioglycollate boils at 55° under 17 mm. pressure.

Thioglycollamide crystallises in white needles, melts at 52°, and is oxidised to dithioglycollamide on exposure to air.

Barium thioglycollate, $Ba(S\cdot CH_2\cdot CO_2)_2Ba,3H_2O$, crystallises in glistening plates; 0·85 part dissolves in 100 parts of water at 17°. The *antimony* salt,  $CO_2H\cdot CH_2\cdot S\cdot Sb<\begin{matrix}S\cdot CH_2\\ | \\ O\cdot CO\end{matrix}$, prepared by the addition of thioglycollic acid (3 mols.) to a solution of antimony chloride (1 mol.) in dilute hydrochloric acid, forms white, monoclinic crystals. The *arsenic* derivative, $As(S\cdot CH_2\cdot CO_2H)_3$, forms rhombic crystals. The *platinum* derivative, $Pt(S\cdot CH_2\cdot CO_2H)_2$, is a red solid. A. McK.

Preparation of Aliphatic Dialdehydes. ALFRED WOHL and H. SCHWEITZER (*Ber.*, 1906, **39**, 890—897).—The authors describe an electrolytic method for the preparation of aliphatic dialdehydes. Potassium β-diethoxypropionate was electrolysed by Crum Brown and Walker's method with a current of 3 amperes and an *E.M.F.* of 8—10 volts, the change represented by the equation occurring: $2KO\cdot CO\cdot CH_2\cdot CH(OEt)_2 = 2K + 2CO_2 + C_2H_4[CH(OEt)_2]_2$. The resulting succintetraethylacetal was proved to be identical with Harries' compound (Abstr., 1902, i, 345).

Potassium γ-diethoxybutyrate, $CH(OEt)_2\cdot CH_2\cdot CH_2\cdot CO_2K$, prepared by the saponification of *β*-cyanopropionic acetal,

$$CH(OEt)_2\cdot CH_2\cdot CH_2\cdot CN,$$

is an amorphous, hygroscopic mass.

Ethyl γ-diethoxybutyrate, $CH(OEt)_2\cdot CH_2\cdot CH_2\cdot CO_2Et$, prepared by the action of ethyl iodide on the potassium salt, is an oil which boils at 113—114° under 10 mm. pressure. When the potassium salt was electrolysed, the double acetal of adipic aldehyde was formed in a 35 per cent. yield. Acraldehyde acetal was, however, also produced, so that the electrolysis also proceeded according to the equation: $2CO_2K\cdot CH_2\cdot CH_2\cdot CH(OEt)_2 =$

$$2K + CO_2H\cdot CH_2\cdot CH_2\cdot CH(OEt)_2 + CH_2{:}CH\cdot CH(OEt)_2.$$

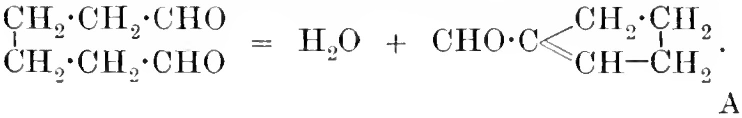
Adipic dialdehyde tetra-acetal, $CH(OEt)_2\cdot[CH_2]_4\cdot CH(OEt)_2$, is a colourless oil which boils at 148° under 10 mm. pressure.

Adipic dialdehyde (*hexane-αζ-dial*), prepared by the action of dilute sulphuric acid on the acetal, boils at 92—94° under 9 mm. pressure. Determinations of its molecular weight by the cryoscopic method indicated that the aldehyde is associated in benzene solution, whereas in aqueous solution it is unimolecular. The residue remaining in the distilling flask after the aldehyde had been distilled off boiled mainly at 130° under 0·2 mm. pressure and was apparently a polymeric form of the aldehyde. Adipic dialdehyde is remarkably stable. When sealed in a glass tube, it may be kept for weeks before it assumes a syrupy consistency; in this respect it differs from octanedial and from succindialdehyde. Adipic dialdehyde is readily resinified when gently warmed with aqueous alkalis. When a solution of nitrophenylhydrazine in acetic acid is added to a solution of adipic dialdehyde in ethyl alcohol, the *bisnitrophenylhydrazone*, $C_{18}H_{20}O_4N_6$, separates in brick-red crystals which melt at 169—170° (corr.). The *disemicarbazone*, $C_8H_{16}O_2N_6$, crystallises in prisms and melts at 206° (corr.). The *dioxime*, $C_6H_{12}O_2N_2$, separates from water in needles and melts at 185—186° (corr.). The *bisulphite* compound,

$$SO_3Na\cdot CH(OH)\cdot[CH_2]_4\cdot CH(OH)\cdot SO_3Na,$$

crystallises in prisms.

When adipic dialdehyde is heated with water for five hours at 110°, it forms *cyclo*pentenealdehyde, which was identified by its semicarbazone, the change being represented by the equation



$$\begin{array}{l}CH_2\cdot CH_2\cdot CHO\\ |\\ CH_2\cdot CH_2\cdot CHO\end{array} = H_2O + CHO\cdot C\begin{array}{l}\diagup CH_2\cdot CH_2\\ \qquad\qquad\ \ |\\ \diagdown CH{-}CH_2\end{array}.$$

A. McK.

Action of Acetone on Alkali Sulphites. VICTOR ROTHMUND (*Monatsh.*, 1905, **26**, 1545—1558. Compare Lumière, Lumière, and Seyewetz, Abstr., 1897, ii, 470; Kerp, Abstr., 1904, i, 713).—The formation of compounds of acetone with sulphurous acid, alkali sulphites, or alkali hydrogen sulphites in aqueous solution is confirmed by means of conductivity measurements and cryoscopic molecular weight determinations. The formation of the compound of acetone and sulphurous acid is represented by the equation: $\overline{SO}_3 + C_3H_6O + H_2O =$

$\overline{SO_3}H(C_3H_6O) + \overline{OH}$. Acetonesulphurous acid is a stronger acid than sulphurous acid, as is shown by the increase in the conductivity of aqueous sulphurous acid which ensues on addition of acetone; the formation of the acetonesulphurous acid takes place slowly, the maximum conductivity being reached in about an hour.

As sulphurous acid is dibasic towards phenolphthalein, but acetonesulphurous, although a stronger acid, is monobasic, a solution of an alkali sulphite, neutral to phenolphthalein, becomes alkaline on addition of acetone. G. Y.

Ketens. II. Dimethylketen. HERMANN STAUDINGER and HELMUT W. KLEVER (*Ber.*, 1906, 39, 968—971. Compare Abstr., 1905, i, 444).—The action of zinc on an ethereal solution of α-bromo*iso*butyryl bromide leads to the formation of *dimethylketen*, $CMe_2\colon CO$, in 38 per cent. yield, which, however, cannot be separated from the solvent by fractional distillation. The use of less volatile solvents is inadmissible, as either the reaction does not take place or the keten produced polymerises. A 28 per cent. yield of the keten is obtained when ethyl acetate is employed as the solvent. To separate the pure keten, the mixed liquids are distilled at −20° under 15—16 mm. pressure, the distillate being collected in a flask at −80°; under these conditions, ethyl acetate is very slightly volatile, and dimethylketen is obtained as a mobile, yellow liquid which is stable at −20° under atmospheric pressure. At the ordinary temperature, it polymerises to a colourless *substance*, which melts at 112—112·5° and appears to be identical with Wedekind and Weisswange's diketone, $(CMe_2\colon CO)_2$. Dimethylketen, which is comparatively stable when dissolved in ether or ethyl acetate, is at once converted by oxygen into a white explosive powder, which is possibly a peroxide. The keten is converted by water or alcohol into *iso*butyric acid and its ester respectively; with aniline, it forms the anilide, and with phenylhydrazine the phenylhydrazide of *iso*butyric acid. With quinone, it forms a colourless additive *compound* which melts at 104·5°. The *compound* with quinoline melts at 152—153° and is stable to dilute acids, but by prolonged boiling with concentrated hydrochloric acid it is decomposed into quinoline and *iso*butyric acid. C. S.

Formation of Formaldehyde during the Destruction of Sugar by Heating. AUGUSTE TRILLAT (*Zeit. Ver. deut. Zuckerind.*, 1906, 95—103. Compare Abstr., 1905, i, 325).—Formaldehyde is formed when sucrose is heated at 100° or any higher temperature, the amount increasing as the temperature rises. If the sucrose is heated in copper foil, it yields as much as 5·7 per cent. of the aldehyde, the increased amount obtained in this way being due to the catalytic action of the metal. The presence of air is not necessary for the formation of formaldehyde, small quantities of which are evolved when sucrose is heated either under oil or in an atmosphere of carbon dioxide.

On heating sugar to incipient carbonisation, it yields the following gaseous products: (1) 0·2—5·7 per cent. of formaldehyde; (2) acetaldehyde; (3) 0·5—1·4 per cent. of benzaldehyde; (4) 0·1—0·5 per cent. of acetone; (5) 0·1—0·5 per cent. of methyl alcohol; (6) 1—3 per cent. of acetic acid; (7) 1—3 per cent. of phenol derivatives.

Caramel, which is obtained by heating sugar with or without the addition of alkali, contains products of polymerisation of formaldehyde.

This formation of formaldehyde explains the disinfecting and deodorising action of the gases formed on burning sugar. T. H. P.

Presence of Formaldehyde in Caramelised Substances.

Auguste Trillat (*Compt. rend.*, 1906, **142**, 454—456. Compare Abstr., 1905, i, 325).—When sugar is heated, formaldehyde occurs, not only in the gaseous products, but also in the residual caramel, the proportion increasing with the temperature at which the caramelisation is effected, as is shown in the following table:

	Temperature of caramelisation.	Formaldehyde in residue.	Formaldehyde liberated.
I.	125°	trace	trace
II.	150	0·090 per cent.	0·300 per cent.
III.	150—180	0·135 ,,	1·100 ,,
IV.	180—200	0·270 ,,	2·200 ,,

Out of five commercial samples of caramel examined three contained appreciable quantities of formaldehyde, 30, 45, and 325 mg. respectively per 100 grams of caramel.

The fermenting properties of sugar are much diminished by partial caramelisation, and caramel acts as an antiseptic or microbicide; the addition of 6 per cent. of sugar caramelised at 200° sterilised a solution of bouillon which had been inoculated with *Bacillus coli communis*, whilst the souring of milk containing the lactic acid ferment was prevented by the addition of 10 per cent. of the caramel.

M. A. W.

Inversion of Starch by Platinum Black.

C. Hugh Neilson (*Amer. J. Physiol.*, 1906, **15**, 412—415).—Platinum black hydrolyses starch, and the sugar formed is probably maltose. The reaction is retarded by the products of hydrolysis. The higher the concentration of the starch solution, the slower the action of the platinum.

W. D. H.

Retrogression and Composition of Natural Starches other than Potato Starch.

Eugène Roux (*Compt. rend.*, 1906, **142**, 95—97).—Potato starch consists of amylose, which only differs from amylocellulose in its greater purity, and a substance to which the name "amylopectin" is given. The latter is dissolved by the action of malt, without production of sugars.

Starches from maize, wheat, rice, peas, and manioc all contain about the same amount of amylose, and they all contain amylopectin.

N. H. J. M.

Grignard's Reaction with Amino-acids. Carl Paal and Erich Weidenkaff (*Ber.*, 1906, **39**, 810—813. Compare Abstr., 1905, i, 436; Süsskind, this vol., i, 133).—The action of magnesium ethyl iodide on ethyl diethylaminoacetate, prepared by the action of diethylamine on ethyl bromoacetate (compare Willstätter, Abstr., 1902, i, 266), leads to the formation of *diethylaminomethyldiethylcarbinol*, $NEt_2 \cdot CH_2 \cdot CEt_2 \cdot OH$, which is obtained as a colourless, viscid oil. It boils at 80—85° under 35 mm. or at 190° under the atmospheric pressure, slowly becomes yellow, is miscible with ether, alcohol, ethyl acetate, or benzene, and dissolves in hot water. It forms stable salts with mineral acids: the *hydrogen sulphate*, $C_{10}H_{23}ON,H_2SO_4$, crystallises in long, colourless needles and melts at 74—76°; the *platinichloride*, $(C_{10}H_{23}ON)_2,H_2PtCl_6$, crystallises in stout, reddish-brown prisms and melts at 130—132°; the *aurichloride*, $C_{10}H_{21}N,HAuCl_4$, crystallises in slender, yellow needles and melts at 112—114°.

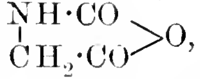
Diphenyldiethylaminomethylcarbinol, $NEt_2 \cdot CH_2 \cdot CPh_2 \cdot OH$, formed by the action of magnesium phenyl bromide on ethyl diethylaminoacetate, is obtained as a crystalline mass which melts at 47—49° and boils at 197° under 40 mm., or with partial decomposition at 280—300° under the atmospheric pressure. The *hydrochloride*, $C_{18}H_{23}ON,HCl$, forms white leaflets and melts at 166—167°; the *platinichloride*,

$$(C_{18}H_{23}ON)_2,H_2PtCl_6,$$

crystallises in yellowish-red plates and melts at 185—186°; the *aurichloride*, $C_{18}H_{23}ON,HAuCl_4$, melts at 125—126°. G. Y.

α-Dimethylaminobutyric Acid. Édouard Duvillier (*Bull. Soc. chim.*, 1906, [iii], **35**, 156—159).—Dimethylamine reacts with α-bromobutyric acid at the atmospheric temperature to form *α-dimethylaminobutyric acid*, which separates, when its aqueous solution is evaporated under reduced pressure at the ordinary temperature over a desiccating agent, in crusts composed of small needles, is hygroscopic, and very soluble in alcohol. The *aurichloride* crystallises in lamellæ, is moderately soluble in water, very soluble in alcohol, and slightly so in ether. The *platinichloride* forms orange-red, monoclinic crystals and is very soluble in water or alcohol. The *hydrochloride* and the *cupric* salt were also prepared. The latter is a convenient means of obtaining the acid in a pure state. Approximate solubilities of the various salts in water or alcohol are given in the original.

T. A. H.

Glycinecarboxylic Acid. Hermann Leuchs (*Ber.*, 1906, **39**, 857—861).—*Glycinecarboxylic anhydride*,  $\begin{matrix} NH \cdot CO \\ | \\ CH_2 \cdot CO \end{matrix}\!\!>\!O$, is obtained when carbethoxyglycyl chloride (Fischer and Otto, Abstr., 1903, i, 608) is heated under reduced pressure at 80—85° for one hour. It crystallises from ethyl acetate in short, six-sided prisms, has a bitter taste, and when heated at 100° evolves carbon dioxide. It dissolves fairly readily in ice-cold water, yielding an acid solution which begins to evolve carbon dioxide at 15°. It also evolves gas when rubbed with twice its weight of water at the ordinary temperature and yields an insoluble powder, $(C_2H_3ON)_x$, with no definite melting point.

With alcoholic hydrogen chloride, the anhydride yields the ethyl glycine hydrochloride and with barium hydroxide solution, barium glycinecarboxylate (Siegfried, this vol., i, 144). J. J. S.

Isomeric Phenylserines. EMIL ERLENMEYER, jun. (and C. BARKOW) (*Ber.*, 1906, **39**, 791—794. Compare Erlenmeyer, Abstr., 1893, i, 36, 166; 1899, i, 759; Erlenmeyer and Früstück, Abstr., 1895, i, 281).—The second possible r-*β-amino-β-phenyl-a-lactic acid*,

$$NH_2\cdot CHPh\cdot CH(OH)\cdot CO_2H,$$

is formed together with small quantities of *r*-*a*-amino-*β*-phenyl-*β*-lactic acid, melting at 187—188°, by the action of ammonia in the cold on sodium oxyphenylacrylate obtained from solid chlorophenyl-lactic or bromophenyl-lactic acid. It crystallises in needles, decomposes at 241°, is only sparingly soluble in water, and forms a deep blue *copper* salt which is almost insoluble in water.

When heated with ammonia, sodium oxyphenylacrylate yields only the *r*-*β*-amino-*β*-phenyl-*a*-lactic acid, melting at 220—221°.

The following derivatives of *β*-amino-*β*-phenyl-*a*-lactic acid are prepared by the action of primary amines on sodium oxyphenylacrylate; the active substances are derived from the *l*-sodium salt having $[a]_D$ $-157\cdot89°$:

r-*β-Anilino-β-phenyl-a-lactic acid*, $NHPh\cdot CHPh\cdot CH(OH)\cdot CO_2H$, prepared from the sparingly soluble sodium salt, crystallises in long, thin needles, melts at 156°, and is soluble in water, or, if prepared from the more soluble sodium phenyloxyacrylate, crystallises in nodules, melts at 158°, and is almost insoluble in water. The l-*acid* melts at 187° and has $[a]_D - 20°$; the *sodium* salt has $[a]_D + 26\cdot68°$.

r-*β-Piperidino-β-phenyl-a-lactic acid*,

$$C_5NH_{10}\cdot CHPh\cdot CH(OH)\cdot CO_2H,$$

melts at 255°. The d-*acid* melts at 256° and has $[a]_D + 43\cdot9°$.

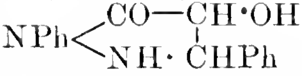
r-*β-Phenetidino-β-phenyl-a-lactic acid*,

$$OEt\cdot C_6H_4\cdot NH\cdot CHPh\cdot CH(OH)\cdot CO_2H,$$

melts at 185°. The l-*acid* melts at 207° and has $[a]_D - 35°$; its *sodium* salt has $[a]_D$ $+ 9\cdot17°$.

Sodium β-phenylhydrazino-β-phenyl-a-lactic acid,

$$NHPh\cdot NH\cdot CHPh\cdot CH(OH)\cdot CO_2Na,$$

yields on acidification the *anhydride*,  $NPh<\begin{array}{l}CO—CH\cdot OH\\ NH\cdot \ CHPh\end{array}$, which melts at 174°; the optically active *sodium* salt has $[a]_D - 197°$, the *anhydride* $[a]_D - 217°$.

The optically active *β*-amino-*β*-phenyl-*a*-lactic acid, corresponding with the racemic acid melting at 241°, is amorphous; its deep blue *copper* salt has $[a]_D + 21\cdot8°$. G. Y.

Carbethoxyl *iso*Cyanate [Ethyl Carbimidecarboxylate]. OTTO DIELS and BERTRAM WOLF (*Ber.*, 1906, **39**, 686—688).—Ethyl nitrogentricarboxylate (Abstr., 1903, i, 324) is converted into ethylene, carbon dioxide, water, and ethyl carbimidecarboxylate when heated with twice its weight of phosphoric oxide at 120°: $N(CO_2Et)_3 = 2C_2H_4 + CO_2 + H_2O + O:C:N\cdot CO_2Et$. *Ethyl carbimidecarboxylate* is collected in a receiver placed in a good freezing mixture and protected from atmospheric moisture. It is a colourless, mobile liquid with a characteristic odour, distils at 115—116° under 781 mm. pressure, and dissolves readily in acetone or ether. It readily reacts with water, yielding carbonyldiurethane (Folin, Abstr., 1897, i, 470), with ammonia yielding ethyl allophanate, and with ethyl alcohol yielding ethyl iminodicarboxylate. J. J. S.

Nitroacetamide. Florian Ratz (*Monatsh.*, 1905, **26**, 1487—1531. Compare Abstr., 1904, i, 298, 857).—The action of alcoholic ammonia on ethyl nitroacetate (Bouveault and Wahl, Abstr., 1904, i, 795), under cooling, leads to the formation of the *ammonium* salt of the ester, $C_4H_6O_4N\cdot NH_4$, which crystallises in slender, white needles, but by the action of an excess of aqueous or alcoholic ammonia the ester is converted into the ammonium salt of nitroacetamide, slowly at the laboratory temperature but more quickly at 100°. The ester interacts in the same way with methylamine or ethylamine, forming the corresponding alkylammonium salts of nitromethyl- or nitroethyl-acetamide; the *methylammonium* salt, $C_4H_{11}O_3N_3$, crystallises from chloroform and melts and decomposes at about 120°.

The action of ethyl iodide on silver nitroacetamide, suspended in acetone at about 5°, leads to the formation of:

(1) *Nitroethylacetamide*, $C_2H_3O_3N_2Et$, which is obtained in a yield not exceeding 30 per cent. of the theoretical; it crystallises in white needles, melts and decomposes at 114°, and is readily soluble in methyl alcohol, ethyl acetate, or acetone, but less so in ethyl alcohol, and only sparingly so in benzene or ether. Ebullioscopic molecular weight determinations show that in alcoholic solution the substance decomposes gradually and evolves a volatile product.

(2) Free nitroacetamide, which is obtained to the extent of 27 per cent. of the silver salt.

(3) An unstable *product*, which separates as a yellow syrup from the final mother liquors on evaporation or on addition of light petroleum.

Nitropropylacetamide, $C_2H_3O_3N_2Pr$, is formed by the action of propyl iodide on silver nitroacetamide to the extent of 32 per cent. of the theoretical; it crystallises in white needles and decomposes at 107°.

Nitroisoamylacetamide, $C_2H_3O_3N_2\cdot C_5H_{11}$, is obtained in a yield of 28 per cent. of the theoretical; it forms glistening, fatty, white scales, melts and decomposes at 100—101°, and has a slight odour of fusel oil. On prolonged heating with water, alcohol, acetone, or other indifferent solvent, nitroethyl-, nitropropyl-, and nitro*iso*amyl-acetamides are decomposed, and, if the solution is distilled, the distillate gives a strong aldehyde reaction. When treated in the same way, nitromethylacetamide gives only a faint aldehyde reaction, but a strong odour of ethyl nitrate. The residue obtained on evaporating the solutions obtained from the ethyl, propyl, and *iso*amyl compounds contains two isomeric oximes:

(1) The *a-oxime*, $OH\cdot N\colon CH\cdot CO\cdot NH_2$, which is the more readily soluble in ethyl acetate, crystallises in white needles or nodular aggregates of needles, melts and evolves a gas at 129°, has a slight acid reaction in aqueous solution, and in moderately concentrated solutions

forms, with silver nitrate, the *additive* compound, $2C_2H_4O_2N_2,AgNO_3$, crystallising in aggregates of slender, white needles. With silver nitrate in presence of 1 mol. of sodium ethoxide, the α-oxime forms the *silver* salt, $C_2H_3O_2N_2Ag$, which crystallises in nodular aggregates of small, stout, light grey needles. On prolonged heating with dilute acids, the α-oxime is hydrolysed with formation of 1 mol. each of ammonia, hydrogen cyanide, carbon dioxide, and water. The hydrolysis with dilute alkali hydroxides takes place more slowly but more completely, the hydrogen cyanide being partially hydrolysed. When heated at 100° with concentrated hydrochloric acid, the α-oxime yields carbon dioxide, ammonia, formic acid, and hydroxylamine. The α-oxime can be prepared by digesting ethyl *iso*nitrosoacetate (Bouveault and Wahl, Abstr., 1904, i, 546) with alcoholic ammonia at 65—70°.

Alkyl derivatives of the α-oxime are prepared by shaking the silver derivative with the alkyl iodides in absolute methyl- or ethyl-alcoholic solution. They are colourless, crystalline substances and are more stable than the parent oxime, as is shown by the diminished rate of hydrolysis with dilute acids or alkali hydroxides.

The *methyl* derivative, $C_2H_3O_2N_2Me$, crystallises in needles and melts at 137·5—138·5°; the *ethyl* derivative, $C_2H_3O_2N_2Et$, forms needles and melts at 125—125·5°; the *propyl* derivative, $C_2H_3O_2N_2Pr$, crystallises in needles and melts at 99·5°; the *amyl* derivative forms glistening, fatty scales and melts at 96°.

(2) The *β-oxime*, $C_2H_4O_2N_2$, which, in most solvents, is much less soluble than the α-oxime, crystallises in nodular aggregates, melts and decomposes at 119—120°, and does not form an insoluble additive compound with silver nitrate, but yields an explosive, yellow, amorphous *silver* salt, $C_2H_3O_2N_2Ag,C_2H_2O_2N_2Ag_2$ (?). The β-oxime is hydrolysed by concentrated hydrochloric acid in the same manner and with formation of the same products as the α-oxime, and is converted into the α-oxime when treated with ammonia.

When oxidised with potassium permanganate in sulphuric acid solution, the α- and β-oximes yield a *product*, $O_2(N{:}CH{\cdot}CO{\cdot}NH_2)_2$ or $NH_2{\cdot}CO{\cdot}CH(NO){\cdot}CH(NO){\cdot}CO{\cdot}NH_2$, which forms a delicate, white, microcrystalline powder, decomposes, when rapidly heated, at 118—122°, and is insoluble in water or organic solvents, but dissolves in dilute alkali hydroxides, from its solution in which no precipitate separates on acidification.

Tables are given showing the comparative rates of hydrolysis, by means of dilute alkali hydroxides, of the two oximes and of nitroacetamide and its alkyl derivatives. The results show that the alkali hydroxide acts not only hydrolytically on the group $-CO{\cdot}NH_2$, but also as a cause of isomeric change. The auto-reduction which takes place in indifferent solvents is effective in alkaline solutions only at the commencement of the reaction.

With bromine water under cooling, nitroethylacetamide forms the *bromo*-derivative, $C_2H_2O_3N_2BrEt$, which is obtained as a fine, white powder, decomposes slowly at the ordinary temperature, or melts and decomposes when heated at 87—88°, and is readily soluble in chloroform or acetone, but less so in methyl or ethyl alcohol, and only sparingly so in water, ether, or benzene.

The author discusses the structure of the alkyl derivatives and the course of their formation by alkylation of nitroacetamide.

Pure bromonitroacetamide is prepared by adding slowly an alkaline alcoholic solution of potassium arsenite to an alcoholic solution of dibromonitroacetamide, treating the potassium derivative so formed with sulphuric acid, and extracting the product with ether. The aqueous solution of the potassium salt is colourless; the *lead* salt forms nodular aggregates of yellowish-white needles; the *silver* salt is obtained as a white, gelatinous precipitate which becomes crystalline.

Bromonitromalonamide and bromonitroacetamide interact in alcoholic solution, slowly at the laboratory temperature, or rapidly when heated, to form nitromalonamide and dibromonitroacetamide.

Nitroacetamide interacts with formaldehyde in 40 per cent. aqueous solution, in presence of ammonia, to form the product $(C_3H_5O_2N_2)_x$, which crystallises in microscopic, spherical aggregates and is insoluble in water, dilute acids, or the usual organic solvents, but dissolves in cold dilute alkali hydroxides or ammonia, from which it is reprecipitated unchanged on acidification. When heated with aqueous potassium hydroxide, it decomposes with evolution of ammonia. The white *silver*, *lead*, and *mercury*, green *copper*, and red *iron* salts are obtained as amorphous precipitates. G. Y.

Action of Esters of certain Dibasic Acids on Magnesium Halogen Derivatives of Primary Aromatic Amines. F. Bodroux (*Compt. rend.*, 1906, **142**, 401—402).—Ethyl oxalate reacts with the magnesium halogen derivative of a primary aromatic amine according to the equation: $C_2O_4Et_2 + 4RNH\cdot MgI = C_2(NHR)_4(OMgI)_2 + 2OEt\cdot MgI$. On treatment with dilute acid, a symmetrically substituted oxamide derivative is obtained, $C_2(NHR)_4(OMgI)_2 + 2HCl = MgCl_2 + MgI_2 + 2NH_2R + C_2O_2(NHR)_2$. In a similar manner, substituted amides are obtained from ethyl succinate, but not from ethyl malonate. The latter, in virtue of its methylenic hydrogen, simply displaces the aromatic amine from the magnesium halogen compound. H. M. D.

Condensation of Acetylenic Nitriles with Alcohols. General Method of Synthesising β-Substituted Derivatives of β-Alkyloxyacrylonitriles. Charles Moureu and I. Lazennec (*Compt. rend.*, 1906, **142**, 338—340. Compare this vol., i, 148).—The acetylenic nitriles, $RC⋮C\cdot CN$, react energetically with sodium methoxide or ethoxide (1 mol.) in the presence of the corresponding alcohol to form a mixture of the β-alkyloxyethylenic nitrile and β-acetal nitrile in varying proportions: thus, phenylpropiolonitrile yields β-phenyl-β-methoxyacrylonitrile (β-methoxycinnamonitrile), $OMe\cdot CPh⁚CH\cdot CN$, and the dimethylacetal of cyanoacetophenone [ββ-dimethoxyphenylacetonitrile], $CPh(OMe)_2\cdot CH_2\cdot CN$; the mixture boils at 165° under 20 mm. pressure, and it is impossible to separate the constituents by fractional distillation. If, however, alcoholic potassium hydroxide replaces the sodium methoxide or ethoxide in the above reaction, the β-alkyloxyethylenic nitrile is the only product of the reaction, and the following compounds were thus prepared: *β-methoxy-β-amylacrylonitrile*, $OMe\cdot C(C_5H_{11})⁚CH\cdot CN$, boiling at 125—131° under 15 mm.

pressure; *β-ethoxy-β-amylacrylonitrile*, $OEt\cdot C(C_5H_{11}):CH\cdot CN$, boiling at 134—135° under 11 mm. pressure; *β-methoxy-β-hexylacrylonitrile*, $OMe\cdot C(C_6H_{13}):CH\cdot CN$, boiling at 138—142° under 14 mm. pressure; *β-ethoxy-β-hexylacrylonitrile*, $OEt\cdot C(C_6H_{13}):CH\cdot CN$, boiling at 141—143° under 14 mm. pressure; *β-methoxy-β-phenylacrylonitrile*, $OMe\cdot CPh:CH\cdot CN$, boiling at 159—166° under 14 mm. pressure; *β-ethoxy-β-phenylacrylonitrile*, $OEt\cdot CPh:CH\cdot CN$, boiling at 166—173° under 12 mm. pressure, and *β-propoxy-β-phenylacrylonitrile*,

$$OPr^{\alpha}\cdot CPh:CH\cdot CN,$$

boiling at 184—190° under 22 mm. pressure. The alkyloxyacetylenic nitriles derived from phenylpropiononitrile are readily hydrolysed by dilute sulphuric acid, forming cyanoacetophenone and an alcohol. The aliphatic derivatives are much more stable; β-ethoxy-β-amylacrylonitrile is only decomposed on prolonged boiling with 50 per cent. sulphuric acid, yielding methyl amyl ketone. M. A. W.

A New Series of Organo-magnesium Compounds containing Ethyl Ether. WLADIMIR TSCHELINZEFF (*Ber.*, 1906, **39**, 773—779).—The amount of ethyl ether which will combine with magnesium propyl iodide and with magnesium *i*-amyl iodide was determined by distilling off the excess of ethyl ether remaining after causing weighed quantities of propyl iodide and magnesium to combine in ethereal solution, and weighing the product; the quantity of ethyl ether combined with the magnesium alkyl iodide points to the existence of derivatives of the type $MgRI,2Et_2O$. That such compounds are formed also appears evident from the fact that, on adding ethyl ether to a solution of propyl or *i*-amyl iodide in benzene containing magnesium, equal quantities of heat are developed for each of the two first mols. of ethyl ether added; the subsequent addition of ether causes little thermal disturbance.

The bearing of these facts on the Grignard syntheses is discussed. Hitherto, the ether derivatives have been assumed to have the composition $RMgI,Et_2O$, based on Blaise's analyses (Abstr., 1901, i, 317). W. A. D.

Influence of Alkyloxy-groups on the Reactivity of α-Halogen Atoms in Aromatic Compounds. GUIDO GOLDSCHMIEDT (*Ber.*, 1906, **39**, 651—652. Compare A. Werner, this vol., i, 180).—Attention is drawn to earlier work (Abstr., 1898, i, 31; 1899, i, 140; 1900, i, 35; 1902, i, 40, 41; 1903, i, 64; also Hertzka, Abstr., 1905, i, 291) in which mention has been made of the influence of alkyloxy-groups on the replacement of α-chlorine atoms by methoxy- or ethoxy-groups. J. J. S.

Nitrostilbenes. FRANZ SACHS and SIEGFRIED HILPERT (*Ber.*, 1906, **39**, 899—906. Compare Sachs and Kempf, Abstr., 1902, i, 682; Sachs and Hilpert, Abstr., 1904, i, 876).—In continuation of their studies on the action of light on chemical compounds, the authors have examined aromatic compounds where the groups $-NO_2$ and $CH:CH$ are in the ortho-position to one another. In the cases examined, no intramolecular reduction and oxidation were observed, as in the case of *o*-nitrobenzaldehyde; neither, as with nitrobenzaldoxime, was any stereochemical transformation observed; on the other hand, polymerisation took place.

When 2 : 4-dinitrostilbene is exposed to light for a month, it undergoes polymerisation to the *compound* $C_{28}H_{20}O_8N_4$, which crystallises from glacial acetic acid in rhombic plates and melts at 199—200°. Determinations of its molecular weight by the ebullioscopic method in acetone showed that the compound has the formula given.

When 2-*nitro*-4-*aminostilbene* is diazotised by Knoevenagel's amyl nitrite method, the *diazo-sulphate*, $C_{14}H_{11}O_6N_3S$, is formed; this crystallises in needles, decomposes at 108°, and explodes at 165°; the *diazo-nitrate*, $C_{14}H_{10}O_5N_4$, crystallises in needles, whilst the *diazo-chloride*, $C_{14}H_{10}O_2N_3Cl$, decomposes at 120°. By the action of sulphuric acid on a boiling solution of 4-diazo-2-nitrostilbene sulphate, 2-*nitrostilbene*, $C_{14}H_{11}O_2N$, is formed; it separates from alcohol in needles and melts at 76°.

4-*Hydrazino*-2-*nitrostilbene*, $C_{14}H_{13}O_2N_3$, prepared by the action of a solution of stannous chloride in hydrochloric acid on a solution of the diazonium sulphate in hydrochloric acid, separates from a mixture of alcohol and light petroleum in red crystals and melts at 125°. The *compound* $C_{21}H_{15}O_6N_5$, formed by the condensation of 4-hydrazino-2-nitrostilbene with 2 : 4-dinitrobenzaldehyde in glacial acetic acid solution, forms dark brown needles and decomposes at 280°.

2-*Aminostilbene*, $C_{14}H_{13}N$, prepared by the reduction of 2-nitrostilbene with stannous chloride in glacial acetic acid solution, crystallises in leaflets and melts at 106°; its ethereal solution exhibits blue fluorescence. Its *acetyl* derivative separates from alcohol in needles and melts at 140°.

2-*Diazo*-4-*nitrostilbene sulphate*, $C_{14}H_9O_6N_3S$, decomposes at 135—157°; the corresponding *chloride* decomposes at 107°.

The *azo*-compound, $C_{24}H_{17}O_3N_3$, formed by coupling 4-diazo-2-nitrostilbene with β-naphthol, melts at 220°; when phenol is substituted for β-naphthol, the *azo*-compound, $C_{20}H_{15}O_3N_3$, is formed; the latter crystallises in dark yellow needles and melts at 192°.

When 2-diazo-4-nitrostilbene sulphate is coupled with aniline, it forms 2-*benzenediazoamino*-4-*nitrostilbene*, $C_{20}H_{16}O_2N_4$, which separates from acetone in reddish-yellow needles and melts at 146°. It undergoes transformation in the presence of aniline hydrochloride into 5′-*nitro*-4-*amino*-2′-*styrylazobenzene*, $C_{20}H_{16}O_2N_4$, which crystallises from light petroleum in bright red needles and melts at 105°; its *hydrochloride* forms needles with the lustre of cantharides and melts at 212°.

The action of light on 2-nitrostilbene yielded resinous substances, the nature of which has not yet been elucidated. A. McK.

Additive Compounds of *p*-Nitrosodimethylaniline with certain Phenols. Henry A. Torrey and J. A. Gibson (*Amer. Chem. J.*, 1906, **35**, 246—253).—It has been shown by Torrey and Hardenbergh (Abstr., 1905, i, 218) that quinhydrone and phenoquinone are dissociated in benzene solution into quinone and quinol, and quinone and phenol, respectively. *p*-Nitrosodimethylaniline forms additive compounds with certain substituted phenols which dissociate in a similar manner. Ebullioscopic determinations of the molecular weight of the compound $NO\cdot C_6H_4\cdot NMe_2,2C_6H_2Cl_3\cdot OH$, described by Edeleanu and Enescu (Abstr., 1896, i, 359), show that this substance is completely dissociated by solvents. The *compound*

$$NO\cdot C_6H_4\cdot NMe_2,2C_6H_2Br_3\cdot OH$$

forms dark red crystals and dissolves in chloroform, alcohol, acetone, benzene, or ether to form green solutions; ebullioscopic determinations show that the compound is completely dissociated when dissolved in benzene. The additive *compound* of salicylic acid and *p*-nitrosodimethylaniline, $NO\cdot C_6H_4\cdot NMe_2,2C_6H_4(OH)\cdot CO_2H$, crystallises in slender, dark red needles, melts at 110°, and dissolves in benzene to form a green solution. The additive compound,

$$NO\cdot C_6H_4\cdot NMe_2,C_6HCl_3(OH)_2$$

(Edeleanu and Enescu, *loc. cit.*), obtained by the union of *p*-nitrosodimethylaniline with trichlororesorcinol, forms dark blue crystals, dissolves in benzene, ether, chloroform, alcohol, or acetone to form green solutions, and is completely dissociated in benzene solution. The tribromoresorcinol *compound*, $2NO\cdot C_6H_4\cdot NMe_2,C_6HBr_3(OH)_2$, is obtained in olive-green crystals, melts at 115°, and is soluble in benzene, chloroform, acetone, alcohol, or ether, forming green solutions. The catechol *compound*, $2NO\cdot C_6H_4\cdot NMe_2,C_6H_4(OH)_2$, forms olive-green crystals, melts and decomposes at 125°, and yields green solutions. The constitution of these additive compounds is discussed.

Attempts to prepare similar compounds with pyrogallol and tetrachlorocatechol were unsuccessful. E. G.

Sulphonation of Thioaniline. OTTO SCHMIDT (*Ber.*, 1906, **39**, 611—616. Compare Merz and Weith, this Journal, 1871, **24**, 566; Nietzki and Bothof, Abstr., 1895, i, 132; Armstrong and Berry, Proc., 1900, **16**, 159).—4 : 4′-*Diaminodiphenylsulphide*-2 : 2′-*disulphonic acid*, $S[C_6H_3(NH_2)\cdot SO_3H]_2$, is prepared (1) by dissolving finely-powdered thioaniline in warm concentrated sulphuric acid and treating the cooled solution with sulphuric acid containing 60 per cent. of sulphur trioxide, or (2) by boiling sodium and chloro-4-nitrobenzene-2-sulphonate with sodium sulphide in aqueous solution and reducing the product with zinc dust and hydrochloric acid. It forms a white powder, is insoluble in water, and when diazotised in dilute hydrochloric acid solution under cooling with ice forms the *bisdiazonium anhydride*, $S\left(C_6H_4{<}\begin{matrix}N_2\\SO_2\end{matrix}{>}O\right)_2$, which, on dilution of its solution in concentrated nitric acid, separates in small, bronze leaflets, detonates at 120—123°, is very sensitive to light, and is insoluble in the usual solvents. It remains unchanged when boiled with water or methyl or ethyl alcohol, and is not decomposed completely when boiled with dilute sulphuric acid for three-quarters of an hour. When treated with sulphur dioxide and copper powder in dilute sulphuric acid solution, made alkaline, evaporated to dryness, and fused with potassium hydroxide, the bisdiazonium anhydride yields thiocatechol, 2 : 2′-dihydroxydiphenyl disulphide, and catechol. G. Y.

Derivatives of Palladosammine. Alexander Gutbier and A. Krell (*Ber.*, 1906, 39, 616—621. Compare this vol., i, 12; Gutbier, Abstr., 1905, i, 584, 876).—Double salts of palladous chloride or bromide, with the hydrochlorides or hydrobromides of benzylamine and dibenzylamine, are formed by mixing the components in hydrochloric acid solution or by adding the base in small quantities to a dilute solution of the palladous salt and recrystallising the precipitate from alcohol.

Benzylamine palladous chloride, $Pd[NH_3(CH_2Ph)Cl]_2Cl_2$, separates from hydrochloric acid in needles or leaflets or from alcohol in glistening, golden-brown leaflets. The *bromide*, $Pd[NH_3(CH_2Ph)Br]_2Br_2$, forms dark red needles or leaflets. *Dibenzylamine palladous chloride*, $Pd[NH_2(CH_2Ph)_2Cl]_2Cl_2$, crystallises in short, brown needles or from alcohol in dark yellowish-red leaflets or long, brown needles. The *bromide*, $Pd[NH_2(CH_2Ph)_2Br]_2Br_2$, separates from hydrochloric acid in glistening, reddish-brown needles or from alcohol in leaflets.

Dibenzylpalladosammine chloride, $Pd(NH_2\cdot CH_2Ph)_2Cl_2$, is formed by the action of an excess of benzylamine on a neutral, aqueous solution of a palladochloride and addition of concentrated hydrochloric acid to the product. It crystallises in yellow leaflets, and when dissolved in ammonia and treated with concentrated hydrochloric acid yields palladosammine chloride. The *bromide*, $Pd(NH_2\cdot CH_2Ph)_2Br_2$, forms small, yellow leaflets, and on treatment with ammonia and concentrated hydrobromic acid yields palladosammine bromide. *Tetrabenzylpalladosammine chloride*, $Pd[NH(CH_2Ph)_2]_2Cl_2$, crystallises from alcohol in glistening, golden leaflets and is converted into palladosammine chloride by ammonia. The *bromide*, $Pd[NH(CH_2Ph)_2]_2Br_2$, forms golden leaflets, and when treated with concentrated hydrobromic acid in hot ammoniacal solution yields palladosammine bromide.

Palladodipyridine chloride (Rosenheim and Maass, Abstr., 1899, i, 163) is formed by the action of pyridine on a palladous chloride or a chloropalladite solution; when heated with ammonia, it evolves pyridine and forms palladosammine chloride. The *bromide*, $Pd(C_5NH_5)_2Br_2$, forms a yellow, microcrystalline precipitate and yields palladosammine bromide when heated with ammonia.

Palladodi-2-methylpyridine chloride, $Pd(C_5NH_4Me)_2Cl_2$, crystallises from alcohol in yellow leaflets, dissolves in an excess of 2-methylpyridine, from its solution in which it is reprecipitated unchanged on addition of concentrated hydrochloric acid, and on treatment with ammonia and hydrochloric acid yields palladosammine chloride. The *bromide*, $Pd(C_5NH_4Me)_2Br_2$, crystallises in yellowish-red leaflets and is converted into palladosammine bromide by treatment with ammonia.

Palladodiquinoline chloride, $Pd(C_9NH_7)_2Cl_2$, is obtained as a yellow precipitate, which is readily soluble in ammonia. The *bromide*, $Pd(C_9NH_7)_2Br_2$, crystallises in reddish-brown, microscopic leaflets. When dissolved in hot aqueous ammonia and treated with concentrated hydrochloric or hydrobromic acid, the palladodiquinoline salts are converted into palladosammine chloride or bromide respectively.

G. Y.

Action of Ethyl Chlorocarbonate on Aromatic Glycines. AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and HENRI BARBIER (*Bull. Soc. chim.*, 1906, [iii], **35**, 123—126).—Phenylglycine reacts with ethyl chlorocarbonate to give the corresponding carbamate,

$$CO_2H\cdot CH_2\cdot NPh\cdot CO_2Et.$$

This is a colourless, viscous liquid, which decomposes when heated and is very soluble in alcohol and ether. The *sodium* and *silver* salts are crystalline; the former melts at 231°. The *amide*, prepared by treating phenylglycineamide with ethyl chlorocarbonate, crystallises from alcohol and melts at 124°, and on prolonged boiling with a dilute solution of sodium hydroxide is transformed partly into phenylglycine and partly into phenylhydantoin. The *ethyl* ester, obtained by treating phenylglycine ester with ethyl chlorocarbonate, is a viscous liquid with a slight pleasant odour, boils at 187—188° under 14 mm. pressure, and decomposes above 300° when heated under atmospheric pressure.

Similar derivatives are obtainable from aromatic glycineamides by the action of ethyl chlorocarbonate. The following substances were prepared in this way.

p-*Tolylurethaneacetamide*, $C_6H_4Me\cdot N(CH_2\cdot CO\cdot NH_2)\cdot CO_2Et$, forms slender, colourless crystals, melts at 153°, and is slightly soluble in alcohol or ether. p-*Phenetidineurethaneacetamide*,

$$OEt\cdot C_6H_4\cdot N(CH_2\cdot CO\cdot NH_2)\cdot CO_2Et,$$

forms slender, colourless needles, melts at 140°, and is easily soluble in alcohol, insoluble in water. *Antipyrineurethaneacetamide*,

$$C_{11}H_{11}ON_2\cdot N(CH_2\cdot CO\cdot NH_2)\cdot CO_2Et,$$

forms colourless needles, melts at 181°, and is soluble in alcohol or water.

T. A. H.

***N*-Methylol Compounds of the Acid Amides.** ALFRED EINHORN (*Annalen*, 1905, **343**, 207—310).—Nitrogen methylol compounds have been obtained by the interaction of acid imides and formaldehyde, but the corresponding reaction has not hitherto been carried out with acid amides. The condensation takes place most readily in an alkaline medium, for example, in the presence of alkali hydroxides, carbonates or cyanides, and organic bases; in many cases, acids will act as condensing agents. An intermediary glycol seems to be formed in the reaction, thus: $R\cdot CO\cdot NH_2 + OH\cdot CH_2\cdot OH = H_2O + R\cdot CO\cdot NH\cdot CH_2\cdot OH$.

The compounds produced are true condensation and not additive products, and when oxidised yield a formyl derivative,

$$R\cdot CO\cdot NH\cdot CHO.$$

These compounds do not yield salts, but are hydrolysed by acids, formaldehyde being produced. Sodium hydrogen sulphite and ammonia behave in a similar manner. They do not yield acyl derivatives, but with acetic anhydride lose water and formaldehyde, methylenedibenzamide being produced; with benzoyl chloride in an alkaline medium, water is eliminated and the methylol compound of methylenedibenzamide formed; the latter readily decomposes into formaldehyde and methylenedibenzamide.

The methylol compounds occasionally interact with acid amides, forming diacylated methylenediamines.

Most monocyclic and aromatic compounds condense with this class of substances very easily, especially hydrocarbons, phenolcarboxylic acids, hydroxy-acids, sulphonic acids, and acylated bases. Generally 1 molecule of the methylol compound replaces one hydrogen of the cyclic nucleus, but occasionally two hydrogens are replaced, diamines being formed.

Methylol compounds of *N*-alkylated acid amides cannot be prepared.

[With Eduard Bischkopff and Bruno Szelinski.]—N-*Methylolbenzamide*, $COPh·NH·CH_2·OH$, prepared by adding a 40 per cent. solution of formaldehyde to a suspension of benzamide in a 3 per cent. solution of potassium carbonate, crystallises in six-sided plates melting at 104—106°; with ammonia, it yields hexamethylenetriamine. N-*Methylolmethylenedibenzamide*, $COPh·NH·CH_2·NBz·CH_2·OH$, prepared from the compound last mentioned by the Schotten-Baumann method or by the action of formaldehyde in the presence of dilute sulphuric acid, forms crystals sintering and then melting at 182·5°; it readily loses formaldehyde, yielding methylenedibenzamide, which can also be prepared from benzamide and formaldehyde in the presence of dilute acids, and crystallises in needles melting at 218—219°. *Methylenedibenzamidecarboxylic acid*, $CH(NHBz)_2·CO_2H$, prepared from benzamide and glyoxylic acid, crystallises in needles melting and decomposing at 234°. *Formylbenzamide* (*benzoylaminoformaldehyde*), $NHBz·CHO$, prepared by oxidising methylolbenzamide by potassium dichromate and sulphuric acid, crystallises in prismatic needles melting at 120°, and from benzene with C_6H_6 in needles melting at 84°; it yields neither a semicarbazone nor a phenylhydrazone; with semicarbazide, the formyl group is eliminated, and with phenylhydrazine *s*-formylphenylhydrazine (m. p. 146°) is produced. 2 : 5-*Diphenyl*-1 : 2 : 4-*triazole*, $C_{14}H_{11}N_3$, crystallises in colourless needles melting at 96—97°, and is volatile without decomposition; the *hydrochloride* crystallises in needles melting and decomposing at 180°, and the *platinichloride* in dark yellow plates decomposing at 218°; the *picrate* crystallises in rhombic plates melting at 148°.

N-*Diethylaminemethylbenzamide* (*benzoyldiethylmethylenediamine*), $COPh·NH·CH_2·NEt_2$, prepared by heating together methylolbenzamide and diethylamine, crystallises in colourless plates melting at 62—64°; the *platinichloride* forms needles melting at 158°, and the *picrate* yellow needles melting at 125°.

N-*Piperidylmethylbenzamide*, $COPh·NH·CH_2·C_5NH_{10}$, prepared from the methylolbenzamide and piperidine, or from benzamide, piperidine, and formaldehyde solution, crystallises in prisms melting at 128—129°.

N-*Benzoylhydroxymethyl*iso*propylbenzylamine*,

$OH·C_6H_2MePr^{\beta}·CH_2·NHBz$ [$Me : Pr : OH : CH_2 = 1 : 4 : 3 : ?$],

prepared from thymol and methylolbenzamide in the presence of hydrochloric acid, crystallises in needles melting at 168—169°. N-*Benzoyl*-o-*dihydroxybenzylamine*, $C_6H_3(OH)_2·CH_2·NHBz$, prepared from methylolbenzamide and *o*-dihydroxybenzene, crystallises in needles melting and decomposing at 270°. N-*Benzoyl*-o-*hydroxymethoxybenzylamine*, $OMe·C_6H_3(OH)·CH_2·NHBz$, prepared from guaiacol and methylolbenzamide, crystallises in rhombic plates melting at 148° and forms a sparingly soluble *sodium* salt; its *acetyl* derivative crystallises in rhombic plates melting at 161°. N-*Benzoyl*-2 : 5-*dihydroxybenzylamine*, prepared from quinol and methylolbenzamide, crystallises in white crystals melting and decomposing at 270°. N-*Dibenzoyl*-1 : 2 : 3-*trihydroxyxylylenediamine*, $C_6H(OH)_3(CH_2 \cdot NHBz)_2$, prepared from pyrogallol and methylolbenzamide, crystallises in colourless prisms or needles melting at 199°.

N-*Benzoyl-3-nitro-4-hydroxybenzylamine*, $NO_2 \cdot C_6H_3(OH) \cdot CH_2 \cdot NHBz$, prepared from *o*-nitrophenol and methylolbenzamide in the presence of sulphuric acid at a low temperature, crystallises in yellow needles melting at 137°. The corresponding *amino*-derivative is obtained by reduction of the nitro-compound with tin and hydrochloric acid, and crystallises in colourless, microscopic needles melting and decomposing at 215°. 3-*Nitro-4-hydroxybenzylamine*,

$$NO_2 \cdot C_6H_3(OH) \cdot CH_2 \cdot NH_2,$$

prepared by hydrolysis of the benzoyl derivative with hydrochloric acid, crystallises in dark orange-red needles, which at 115° lose water, becoming light yellow, and melt at 225°. 3-*Amino-4-hydroxybenzylamine dihydrochloride*, prepared by reducing the compound last mentioned, forms grey crystals. N-*Benzoyl-5-nitro-2-hydroxybenzylamine*,

$$NO_2 \cdot C_6H_3(OH) \cdot CH_2 \cdot NHBz,$$

prepared from *p*-nitrophenol and methylolbenzamide in the presence of sulphuric acid, crystallises in yellow needles melting at 217—218°. On hydrolysis with alcoholic potash, it yields the corresponding *base*, which crystallises in golden-yellow leaflets melting and decomposing at 250°; when treated with nitrous acid, it yields the corresponding benzyl alcohol (m. p. 126°); the *hydrochloride* of the base crystallises in yellow needles melting and decomposing at 250°.

3-Nitro-2-hydroxybenzyl chloride does not yield benzylamine when treated either with ammonia or potassium phthalimide, but it reacts with diethylamine and ethylaniline. 5-*Nitro-2-hydroxybenzyldiethylamine*, $NO_2 \cdot C_6H_3(OH) \cdot CH_2 \cdot NEt_2$, crystallises in pale yellow needles melting at 68—69°; its *hydrochloride* forms colourless crystals melting and decomposing at 197°. *Phenyl-5-nitro-2-hydroxybenzylethylamine*, $NO_2 \cdot C_6H_3(OH) \cdot CH_2 \cdot NEtPh$, forms yellow prisms sintering and then melting at 126°. When reduced, it forms the corresponding *amino*-compound.

N-*Benzoyl-5-amino-2-hydroxybenzylamine*,

$$NH_2 \cdot C_6H_3(OH) \cdot CH_2 \cdot NHBz,$$

prepared by reducing the corresponding nitro-compound, crystallises in colourless needles melting at 186°. Its *hydrochloride* melts and decomposes at 157°; when hydrolysed, it yields the *dihydrochloride*, $HCl,NH_2 \cdot C_6H_3(OH) \cdot CH_2 \cdot NH_2,HCl$, crystallising in white needles melting above 300°.

N-*Benzoyl-β-hydroxynaphthylmethylamine*, $OH \cdot C_{10}H_6 \cdot CH_2 \cdot NHBz$, prepared from β-naphthol and methylolbenzamide, crystallises in colourless prisms melting at 186°. N-*Benzoyl-2-hydroxyquinolylmethylamine*, $OH \cdot C_9NH_5 \cdot CH_2 \cdot NHBz$, from 2-hydroxyquinoline and methylolbenzamide, forms crystals melting at 186°; its *hydrochloride* crystallises in lemon-yellow prisms melting and decomposing at 151°. N-*Benzoylbenzylaminecarboxylic* [*ω-benzoylamino*-m-*toluic*] *acid*, $NHBz \cdot CH_2 \cdot C_6H_4 \cdot CO_2H$, forms crystals melting at 186°.

[With Gustav Schupp.]—N-*Methylolsalicylamide*,

$OH\cdot C_6H_4\cdot CO\cdot NH\cdot CH_2\cdot OH$,

prepared from salicylamide and formaldehyde in an alkaline medium, crystallises in prismatic needles melting at 126—128°; if excess of formaldehyde is used, and potassium cyanide be used as condensing agent, the *compound* $C_{15}H_{16}O_5N_2$, crystallising in prismatic needles melting at 114—116°, is obtained. It is soluble in alkali hydroxides and gives a violet coloration with ferric chloride. *Methylenedisalicylamide*, $CH_2(NH\cdot CO\cdot C_6H_4\cdot OH)_2$, prepared from methylolsalicylamide and salicylamide, crystallises in needles melting at 195—197° and is soluble in alkali hydroxides. *Dibenzoylmethylenesalicylamide*, $CH_2(NH\cdot CO\cdot C_6H_4\cdot OBz)_2$, prepared from methylenedisalicylamide and benzoyl chloride in the presence of pyridine, crystallises in prismatic needles melting at 182—183°. *Methylenebenzoylsalicylamide*,

$NHBz\cdot CH_2\cdot NH\cdot CO\cdot C_6H_4\cdot OH$,

prepared from methylolsalicylamide and benzamide, crystallises in prismatic needles sintering and then melting at 151—153°. N-*Piperidylmethylsalicylamide*, $OH\cdot C_6H_4\cdot CO\cdot NH\cdot CH_2\cdot C_5NH_{10}$, prepared from salicylamide, piperidine, and formaldehyde, crystallises in microscopic needles melting at 93—95°. When methylolsalicylamide is benzoylated in pyridine, *dibenzoylsalicyliminodimethyl ether*, $(OH\cdot C_6H_4\cdot CO\cdot NBz\cdot CH_2)_2O$, is obtained, crystallising in prismatic needles melting at 184—185°. N-*Salicylhydroxymethyl*iso*propylbenzylamine*, $OH\cdot C_6H_2MePr^{\beta}\cdot CH_2\cdot NH\cdot CO\cdot C_6H_4\cdot OH$, prepared from methylolsalicylamide and thymol, crystallises in needles melting at 170—172°. *Di-N-salicyl*-1 : 2-*dihydroxyxylylenediamine*,

$C_6H_2(OH)_2(CH_2\cdot NH\cdot CO\cdot C_6H_4\cdot OH)_2$,

prepared from methylolsalicylamide and *o*-dihydroxybenzene, is a crystalline powder melting at 200—203° and soluble in, but decomposed by, alkali hydroxides. *Di-N-salicyl*-1 : 4-*dihydroxyxylylenediamine*, prepared from quinol, is a crystalline powder decomposing at 250—252°. N-*Salicyl*-1 : 2 : 3-*trihydroxybenzylamine*,

$C_6H_2(OH)_3\cdot CH_2\cdot NH\cdot CO\cdot C_6H_4\cdot OH$,

prepared from pyrogallol and methylolsalicylamide, crystallises in needles melting and decomposing at 195—197°.

[With Carl Ladisch.]—*Methylolformamide*, $HCO\cdot NH\cdot CH_2\cdot OH$, prepared from formaldehyde and formamide in an alkaline medium, is a colourless oil. When condensed with *p*-nitrophenol, N-*formylnitrohydroxybenzylamine*, $OH\cdot C_6H_3(NO_2)\cdot CH_2\cdot NH\cdot CHO$, is obtained as yellow, prismatic needles melting and decomposing at 236°.

Methylolacetamide, $NHAc\cdot CH_2\cdot OH$, prepared from acetamide and formaldehyde in an alkaline medium, forms crystals melting at 50—52°. N-*Diacetylnitrohydroxyxylylenediamine*,

$OH\cdot C_6H_2(NO_2)(CH_2\cdot NHAc)_2$,

prepared from methylolacetamide and *p*-nitrophenol in the presence of concentrated sulphuric acid, crystallises in yellow prisms or leaflets melting at 196°.

[With Eduard Spröngerts.]—N-*Methylol*iso*valeramide*,

$CHMe_2\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot OH$,

prepared from *iso*valeramide and formaldehyde in the presence of potassium carbonate, crystallises in needles melting at 76—79°.

Methylenediisovaleramide, $CH_2(NH\cdot CO\cdot CH_2\cdot CHMe_2)_2$, prepared by heating methylol*iso*valeramide at 90°, or from *iso*valeramide and methylol*iso*valeramide, crystallises in needles melting at 191°. N-*Diethylaminomethylisovaleramide*, $CHMe_2\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot NEt_2$, prepared from diethylamine, *iso*valeramide, and formaldehyde, is a pale yellow oil; the *picrate* crystallises in yellow needles melting at 132°. N-*Piperidylmethylisovaleramide*, $CHMe_2\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot C_5NH_{10}$, prepared from *iso*valeramide, piperidine, and formaldehyde, is a pale yellow, thick oil yielding a *picrate* melting at 183°.

N-*Methyloldiethylacetamide*, $CHEt_2\cdot CO\cdot NH\cdot CH_2\cdot OH$, prepared from diethylacetamide and formaldehyde in the presence of alkali, crystallises in prisms melting at 87—88°. N-*Diethylaminomethyldiethylacetamide*, $CHEt_2\cdot CO\cdot NH\cdot CH_2\cdot NEt_2$, prepared from diethylacetamide, diethylamine, and formaldehyde, is a semi-solid mass; the *acid tartrate* crystallises with $2H_2O$ and melts at 67°. N-*Piperidylmethyldiethylacetamide*, $CHEt_2\cdot CO\cdot NH\cdot CH_2\cdot C_5NH_{10}$, prepared from diethylacetamide, piperidine, and formaldehyde, crystallises in needles melting at 125°; its *hydrochloride* melts at 121° and its *hydrobromide* at 145°.

s-N-*Dimethyloldiethylmalonamide*, $CEt_2(CO\cdot NH\cdot CH_2\cdot OH)_2$, prepared from diethylmalonamide and formaldehyde in the presence of barium hydroxide, crystallises in leaflets melting at 141°. s-N-*Diformyldiethylmalonamide*, $CEt_2(CO\cdot NH\cdot CHO)_2$, prepared from the compound last mentioned by oxidation with chromic acid mixture, forms granular crystals melting at 178°. *Mono-N-diethylaminomethyldiethylmalonamide*, $NH_2\cdot CO\cdot CEt_2\cdot CO\cdot NH\cdot CH_2\cdot NEt_2$, prepared from diethylmalonamide, diethylamine, and formaldehyde, forms crystals melting at 109°; at the same time, the *di-N-ethylaminomethyldiethylmalonamide*,

$$CEt_2(CO\cdot NH\cdot CH_2\cdot NEt_2),$$

is formed and is separated from the mono-derivative by taking advantage of its solubility in petroleum; it crystallises in needles melting at 86°. *Mono-N-piperidylmethyldiethylmalonamide*,

$$NH_2\cdot CO\cdot CEt_2\cdot CO\cdot NH\cdot CH_2\cdot C_5NH_{10},$$

prepared from diethylmalonamide, piperidine, and formaldehyde, crystallises in needles melting at 136—141° and is insoluble in carbon disulphide; the corresponding *di-derivative*,

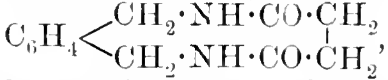
$$CEt_2(CO\cdot NH\cdot CH_2\cdot C_5NH_{10})_2,$$

which is formed at the same time as the compound last mentioned, crystallises in plates melting at 115—119° and is soluble in carbon disulphide.

[With CARL LADISCH.]—N-*Dimethylolsuccinamide*,

$$C_2H_4(CO\cdot NH\cdot CH_2\cdot OH)_2,$$

prepared from succinamide and formaldehyde in the presence of aqueous potassium carbonate, forms crystals melting and decomposing at 167°. *Succinylxylylenediamine*,



$$C_6H_4<\begin{matrix}CH_2\cdot NH\cdot CO\cdot CH_2\\ \quad\quad\quad\quad\quad\quad\quad | \\ CH_2\cdot NH\cdot CO\cdot CH_2\end{matrix},$$

prepared from dimethylolsuccinamide and benzene in presence of concentrated sulphuric acid, forms a yellow, amorphous solid melting and decomposing at about 225°. N-*Succinyl-5-nitro-2-hydroxybenzylamine*,

$$C_2H_4[CO\cdot NH\cdot CH_2\cdot C_6H_3(NO_2)\cdot OH]_2,$$

prepared from *p*-nitrophenol and methylolsuccinamide in the presence of concentrated sulphuric acid, forms white crystals melting at 257°

and is decomposed by heating with hydrochloric acid into succinic acid and *m*-nitro-*o*-hydroxybenzylamine. N-*Succinyl-β-hydroxynaphthylmethylamine*, $C_2H_4(CO\cdot NH\cdot CH_2\cdot C_{10}H_6\cdot OH)_2$, prepared from β-naphthol and dimethylolsuccinamide in the presence of dilute alcoholic hydrochloric acid, crystallises in needles melting at 222—224°.

N-*Methylolchloroacetamide*, $CH_2Cl\cdot CO\cdot NH\cdot CH_2\cdot OH$, prepared from monochloroacetamide and formaldehyde in the presence of hydrochloric acid, crystallises in colourless prisms melting at 91—102°. N-*Methyloltrichloroacetamide*, $CCl_3\cdot CO\cdot NH\cdot CH_2\cdot OH$, prepared from trichloroacetamide and formaldehyde in the presence of dilute sulphuric acid, crystallises in needles melting at 99—100°. N-*Methylolbromoacetamide*, prepared from bromoacetamide and formaldehyde in the presence of hydrochloric acid, forms crystals melting at 94—95°. N-*Methylol-α-bromopropionamide*, $CH_3\cdot CHBr\cdot CO\cdot NH\cdot CH_2\cdot OH$, prepared from α-bromopropionamide and formaldehyde, crystallises in prismatic needles melting at 93—95° and decomposes when heated with the elimination of formaldehyde. N-*Methyloliodoacetamide*, prepared from iodoacetamide and formaldehyde, crystallises in leaflets melting at about 130°.

[With Theodor Mauermayer.]—*Formylchloroacetamide*,

$$CH_2Cl\cdot CO\cdot NH\cdot CHO,$$

prepared by oxidising *N*-methylchloroacetamide, forms crystals melting at 89—90°, yields no hydrogen sulphite compound, but reduces ammoniacal silver nitrate. *Methylenebischloroacetamide*,

$$CH_2(NH\cdot CO\cdot CH_2Cl)_2,$$

prepared from methylolchloroacetamide and concentrated sulphuric acid, crystallises in leaflets melting at 175°. N-*Chloroacetylhydroxymethyl*iso*propylbenzylamine*, $OH\cdot C_6H_2MePr^{\beta}\cdot CH_2\cdot NH\cdot CO\cdot CH_2Cl$, prepared from thymol and methylolchloroacetamide, crystallises in needles melting at 152—153°. N-*Chloroacetyl*-3-*nitro*-4-*hydroxybenzylamine*, $OH\cdot C_6H_3(NO_2)\cdot CH_2\cdot NH\cdot CO\cdot CH_2Cl$, prepared from *o*-nitrophenol and methylolchloroacetamide in the presence of sulphuric acid, crystallises in pale yellow needles melting at 106—107°. The corresponding 5-*nitro*-2-*hydroxy*-compound is prepared in a similar manner, using *p*-nitrophenol, and crystallises in needles melting at 185—186°, and when heated with diethylamine is converted into N-*diethylglycyl*-5-*nitro*-2-*hydroxybenzylamine hydrochloride*,

$$OH\cdot C_6H_3(NO_2)\cdot CH_2\cdot NH\cdot CO\cdot CH_2\cdot NEt_2,HCl,$$

which crystallises in needles melting at 199°; the free *base* crystallises in yellow needles melting at 150°. N-*Bischloroacetyl*-1-*nitro*-4-*ethoxyxylylenediamine*, $NO_2\cdot C_6H_2(OEt)\cdot(CH_2\cdot NH\cdot CO\cdot CH_2Cl)_2$, prepared from *p*-nitrophenetole and methylolchloroacetamide in the presence of sulphuric acid, crystallises in needles melting at 184°. 1-*Nitro*-4-*ethoxyxylylene diamine hydrochloride*, $NO_2\cdot C_6H_2(OEt)(CH_2\cdot NH_2,HCl)_2$, prepared by boiling the compound last mentioned with hydrochloric acid, crystallises in needles which carbonise without melting and yields on oxidation with permanganate a *compound* melting at 176°, probably 1-*nitro*-4-*phenetoledicarboxylic acid*. *Bisdiethylglycyl*-1-*nitro*-4-*ethoxyxylylenediamine*, $NO_2\cdot C_6H_2(OEt)(CH_2\cdot NH\cdot CO\cdot CH_2\cdot NEt_2)_2$, prepared from bischloroacetylnitroethoxyxylylenediamine and diethylamine, crystallises in needles melting at 118—119°. N-*Chloroacetyl*-1 : 2-*dihydroxybenzyl*-

amine, $C_6H_3(OH)_2\cdot CH_2\cdot NH\cdot CO\cdot CH_2Cl$, prepared from *o*-dihydroxybenzene and methylolchloroacetamide, crystallises in colourless prisms melting at 140—141°. 1 : 2-*Dihydroxybenzylamine hydrochloride,* $C_6H_3(OH)_2\cdot CH_2\cdot NH_2,HCl$, prepared by boiling chloroacetyldihydroxybenzylamine with dilute hydrochloric acid, crystallises in needles melting at 169°. The *borate* of N-*diethylglycyl*-1 : 2-*dihydroxybenzylamine,* $C_6H_3(OH)_2\cdot CH_2\cdot NH\cdot CO\cdot CH_2\cdot NEt_2,HBO_2$, is formed when the product of the interaction of chloroacetyldihydroxybenzylamine and diethylamine is treated with an alcoholic solution of boric acid, and is a white, amorphous powder decomposing without melting. N-*Chloroacetyl*-1-*hydroxy*-2-*methoxybenzylamine,*

$$OH\cdot C_6H_3(OMe)\cdot CH_2\cdot NH\cdot CO\cdot CH_2Cl,$$

prepared from guaiacol and methylolchloroacetamide in the presence of sulphuric acid, crystallises in needles melting at 116—119°. N-*Bischloroacetyl*-1 : 4-*dihydroxyxylylenediamine,*

$$C_6H_2(OH)_2(CH_2\cdot NH\cdot CO\cdot CH_2Cl)_2,$$

prepared from quinol and methylolchloroacetamide, crystallises in brown needles melting at 235°. N-*Bischloroacetyl*-1 : 2 : 3-*trihydroxyxylylenediamine,* $C_6H(OH)_3(CH_2\cdot NH\cdot CO\cdot CH_2Cl)_2$, prepared from pyrogallol and methylolchloroacetamide, crystallises in needles melting at 190—191°. m-*Chloroacetylbenzylaminecarboxylic* [*ω-chloroacetylamino*-m-*toluic*] *acid,* $CH_2Cl\cdot CO\cdot NH\cdot CH_2\cdot C_6H_4\cdot CO_2H$, prepared from methylolchloroacetamide and benzoic acid, crystallises in needles melting at 176°, and when boiled with hydrochloric acid yields *m*-benzylaminecarboxylic acid. *Ethyl* m-*chloroacetylbenzylaminecarboxylate,* $CH_2Cl\cdot CO\cdot NH\cdot CH_2\cdot C_6H_4\cdot CO_2Et$, prepared from the acid last mentioned, crystallises in needles melting at 86—87°. *Ethyl* m-N-*piperidylglycylbenzylaminecarboxylate,*

$$C_5NH_{10}\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot C_6H_4\cdot CO_2Et,$$

prepared by treating the ester with piperidine, is a thick oil, the *hydrochloride* of which crystallises in prisms melting at 135—136°; the *hydriodide* crystallises in needles melting at 128°, and the *periodide* crystallises in reddish-brown needles melting at 171°. *Ethyl* m-N-*diethylglycylbenzylaminecarboxylate,*

$$NEt_2\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot C_6H_4\cdot CO_2Et,$$

prepared from diethylamine and ethyl chloroacetylbenzylaminecarboxylate, is an oil; its *picrate* crystallises in golden-yellow leaflets melting at 146°. N-*Dichloroacetyl*-o-*hydroxyxylylenediaminecarboxylic acid,*

$$OH\cdot C_6H_2(CH_2\cdot NH\cdot CO\cdot CH_2Cl)_2\cdot CO_2H,$$

prepared from salicylic acid and methylolchloroacetamide, crystallises in needles melting at 196—197°. N-*Chloroacetyl*-4-*acetylaminobenzylamine,* $NHAc\cdot C_6H_4\cdot CH_2\cdot NH\cdot CO\cdot CH_2Cl$, prepared by condensing methylolchloroacetamide and acetanilide by the aid of sulphuric acid, crystallises in needles melting at 206—207° and is hydrolysed to *p*-aminobenzylamine. N-*Diethylglycyl*-4-*acetylaminobenzylamine,*

$$NHAc\cdot C_6H_4\cdot CH_2\cdot NH\cdot CO\cdot CH_2\cdot NEt_2,$$

prepared by the action of diethylamine on the compound last mentioned, crystallises in leaflets melting at 116—117°. N-*Chloroacetyl*-4-*acetylamino*-1-*ethoxybenzylamine,*

$$NHAc\cdot C_6H_3(OEt)\cdot CH_2\cdot NH\cdot CO\cdot CH_2Cl,$$

prepared from acetylphenetidine and methylolchloroacetamide, crystallises in needles melting at 179° and is hydrolysed to 4-*amino*-1-*ethoxybenzylamine dihydrochloride*, which crystallises in needles melting and decomposing at 276°. The free *base* is an oil boiling at 300° (not undecomposed), and absorbs carbon dioxide from the air. N-*Diethylglycyl*-4-*acetylamino*-1-*ethoxybenzylamine*,

$$\text{NHAc·C}_6\text{H}_3\text{(OEt)·CH}_2\text{·NH·CO·CH}_2\text{·NEt}_2,$$

prepared by the action of diethylamine on the corresponding chloroacetyl derivative, crystallises in leaflets melting at 122°; the *hydrochloride* forms hygroscopic leaflets. N-*Chloroacetyl*-4-*lactylamino*-1-*ethoxybenzylamine*,

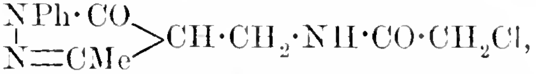
$$\text{OH·CHMe·CO·NH·C}_6\text{H}_3\text{(OEt)·CH}_2\text{·NH·CO·CH}_2\text{Cl},$$

prepared from methylolchloroacetamide and lactyl-*p*-phenetidine, crystallises in needles melting at 116°. N-*Diethylglycyl*-4-*lactylamino*-1-*ethoxybenzylamine*,

$$\text{OH·CHMe·CO·NH·C}_6\text{H}_3\text{(OEt)·CH}_2\text{·NH·CO·CH}_2\text{·NEt}_2,$$

prepared from the compound last mentioned and diethylamine, crystallises in scales melting at 131—132°.

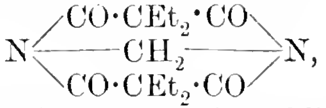
4-*Chloroacetylaminomethyl*-1-*phenyl*-3-*methylpyrazolone*,



$$\begin{array}{l}\text{NPh·CO}\\ \ |\\ \text{N}{=}\text{CMe}\end{array}\!\!>\text{CH·CH}_2\text{·NH·CO·CH}_2\text{Cl},$$

prepared from methylolchloroacetamide and 1-phenyl-3-methylpyrazolone, crystallises in colourless needles melting at 187°.

N-Methyloltrichloroacetamide and concentrated sulphuric acid yield *methylenebistrichloroacetamide*, $\text{CH}_2\text{(NH·CO·CCl}_3)_2$, which crystallises in colourless leaflets melting at 197°. When treated at a low temperature with 50 per cent. potassium hydroxide, it is converted into methylenediamine, $\text{CH}_2\text{(NH}_2)_2$, which, however, could not be isolated, as it readily decomposes into formaldehyde and ammonia; it was obtained as a *dibenzoyl* derivative melting at 220°. With diethylmalonic chloride it does not give the expected diethylmalonylmethylenediamine, but *bisdiethylmalonylmethylenediamine*,



and *methylenebisdiethylmalonamic acid*, $\text{CH}_2\text{(NH·CO·CEt}_2\text{·CO}_2\text{H)}_2$. The first compound crystallises in quadratic leaflets melting at 138°; the second, which is precipitated from the solution of the first by hydrochloric acid, crystallises in scales melting at 189—190°, and when heated above its melting point is converted into *bisdiethylacetylmethylenediamine*, $\text{CH}_2\text{(NH·CO·CHEt}_2)_2$, with the elimination of carbon dioxide.

K. J. P. O.

Benzoylphenylcarbamide. ERNST MOHR (*J. pr. Chem.*, 1906, [ii], **73**, 207. Compare Abstr., 1905, i, 890).—Attention is drawn to Stieglitz and Earle's explanation of the formation of benzoylphenylcarbamide from benzoylchloroamide (Abstr., 1904, i, 39, 40).

G. Y.

Hofmann's Reaction. II. ERNST MOHR (*J. pr. Chem.*, 1906, [ii], **73**, 177—191. Compare Abstr., 1905, i, 274, 890; Dam and Aberson, Abstr., 1901, ii, 88).—When shaken with 0·3*N* aqueous baryta at

10°, phenylcarbimide dissolves completely in a few minutes, and the solution, which does not give a coloration with bleaching powder, deposits barium phenylcarbamate. This is obtained in a yield of 65—75 per cent. of the theoretical if 1·1 equivalents of baryta are employed, 2 vols. of alcohol added, and the mixture cooled with ice. The product is slightly red and contains traces of carbanilide.

Barium phenylcarbamate, $(NHPh\cdot CO_2)_2Ba.2H_2O$, has, when freshly prepared, an odour of aniline, which disappears when the substance is dried over sulphuric acid in a vacuum; when heated at 100—110°, the salt decomposes, leaving a residue of barium carbonate. In aqueous or slightly alkaline solution at the laboratory temperature, the phenylcarbamate decomposes slowly, forming aniline, carbon dioxide, and barium carbonate; thus, decomposition takes place immediately if the phenylcarbamate is dissolved in warm water, but is hindered by the presence of an excess of baryta. On addition of hydrochloric or acetic acid or carbon dioxide to its aqueous solution, the phenylcarbamate decomposes immediately, forming aniline and carbon dioxide. No odour of phenylcarbimide could be observed.

The action of methyl iodide and methyl alcohol on barium phenylcarbamate leads to the formation of aniline, dimethylaniline and its methiodide, and probably of methylaniline.

Phenylcarbimide is decomposed only extremely slowly when shaken with 0·98N hydrochloric acid at 0°. G. Y.

Synthesis of Three Secondary Dimethyl*cyclo*hexanols. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1906, **142**, 553—555. Compare Abstr., 1904, i, 156; 1905, i, 275).—When 1 : 2 : 4-xylenol is directly hydrogenated in the presence of reduced nickel at 190—200°, two-thirds of the phenol is reduced to *o*-xylene, the remaining one-third to a mixture of three parts of the corresponding dimethyl*cyclo*hexanol and one of the dimethyl*cyclo*hexanone. 1 : 2-*Dimethyl*-4-cyclo*hexanol* is a colourless liquid with an odour similar to that of *cyclo*hexanol; it boils at 189° (corr.), has a sp. gr. 0·9261 at 0°/4° or 0·9073 at 16°/4°, n_D 1·458 at 16°, forms a *phenylcarbamate* crystallising in needles or rhombic plates which melt at 119°, and when oxidised by chromic acid or heated with copper at 300° yields 1 : 2-*dimethyl*-4-cyclo*hexanone*, a colourless liquid with an agreeable odour, which boils at 187° (corr.) and forms a crystalline derivative with sodium hydrogen sulphite and a crystalline *semicarbazone* melting and decomposing at 175°.

1 : 3-*Dimethyl*-4-cyclo*hexanol* is the chief product obtained by the direct hydrogenation of 1 : 3 : 4-xylenol in the presence of reduced nickel at 190—200°; it is a colourless liquid which boils at 176·5° (corr.), has a sp. gr. 0·9235 at 0°/4° or 0·9119 at 16°/4°, and n_D 1·458 at 16°; the *phenylcarbamate* forms brilliant prisms melting at 96°; the *acetate* is a colourless liquid with a penetrating and agreeable odour, which boils at 198° (corr.), has a sp. gr. 0·9405 at 14°/0°, and n_D 1·442 at 14°; the corresponding dimethyl*cyclo*hexene (compare Abstr., 1905, i, 588) is obtained by the action of zinc chloride on the alcohol; it has a sp. gr. 0·8122 at 12°/4° and n_D 1·451 at 12°; and the corresponding 1 : 3-dimethyl-4-*cyclo*hexanone is a colourless liquid which boils at

176·5° (corr.), has a sp. gr. 0·9210 at 0°/4° or 0·9124 at 16°/4°, n_D 1·446 at 16°, and forms a crystalline derivative with sodium hydrogen sulphite and a *semicarbazone* which melts at 190°.

1 : 4-Dimethyl-2-*cyclo*hexanol is obtained by the direct hydrogenation of 1 : 4 : 2-xylenol and the yield is 90 per cent.; it is a colourless liquid with an agreeable odour, which boils at 178·5° (corr.), has a sp. gr. 0·9218 at 0°/4° or 0·9037 at 16°/4°, and n_D 1·455 at 16°; the *phenylcarbamate* melts at 115°. 1 : 4-Dimethyl-2-*cyclo*hexanone is a colourless liquid which boils at 176° (corr.) and forms a crystalline compound with sodium hydrogen sulphite and a *semicarbazone* which melts at 155°. M. A. W.

Synthesis of Tertiary Alcohols derived from 1-Methyl-4-*cyclo*hexanone. Paul Sabatier and Alphonse Mailhe (*Compt. rend.*, 1906, **142**, 438—440. Compare Abstr., 1905, i, 275, 587, 706).—1 : 4-Dimethyl*cyclo*hexene (Abstr., 1905, i, 588) has a sp. gr. 0·8207 at 0°/4° or 0·8111 at 14°/4° and n_D 1·451 at 14°; 1-*methyl*-4-*ethyl*-4-cyclo*hexanol*, prepared by the action of magnesium ethyl iodide on 1-methyl-4-*cyclo*hexanone, is a liquid with an agreeable odour, boils at 89° under 20 mm. pressure, has a sp. gr. 0·9225 at 0°/4° or 0·9130 at 16°/4° and n_D 1·460 at 16°. The *acetate* boils at 197°, the *phenylcarbamate* crystallises in brilliant needles which melt at 123°. 1-*Methyl*-4-*ethyl*cyclo*hexene*, obtained by the dehydrating action of zinc chloride, boils at 149° (corr.), has a sp. gr. 0·8278 at 0°/4° or 0·8169 at 16°/4°, n_D 1·453 at 16°, and yields 1-methyl-4-ethyl*cyclo*hexane on direct hydrogenation in the presence of reduced nickel; this hydrocarbon boils at 147° (corr.), not at 150° as originally stated (Sabatier and Senderens, Abstr., 1901, i, 459), and has a sp. gr. 0·7884 at 15°/4° and n_D 1·435 at 15°.

The chief products of the action of magnesium propyl iodide on 1-methyl-4-*cyclo*hexanone are propylene and 1-methyl-4-*cyclo*hexanol (compare Abstr., 1905, i, 706), together with a small quantity of 1-*methyl*-4-*propyl*-4-cyclo*hexanol*, which is a colourless liquid smelling like camphor, and boiling at 97° under 20 mm. pressure; the corresponding cyclo*hexene*, $C_{10}H_{18}$, boils at 168—170° (corr.), has a sp. gr. 0·8387 at 0°/4° or 0·8270 at 16°/4°, and n_D 1·455 at 16°.

1-*Methyl*-4-iso*propyl*-4-cyclo*hexanol*, obtained in small quantity by the action of magnesium *iso*propyl iodide on 1-methyl-4-*cyclo*hexanone, boils at 94° under 20 mm. pressure, and the corresponding *cyclo*hexene boils at 166—167° and is identical with menthene.

1-*Methyl*-4-iso*amyl*-4-cyclo*hexanol* is a colourless liquid which boils at 125° under 6 mm. pressure, has a sp. gr. 0·9043 at 0°/4° or 0·8937 at 16°/4°, and n_D 1·4615 at 16°, and yields 1-*methyl*-4-iso*amyl*cyclo*hexene*, $C_{12}H_{22}$, which is a liquid with an agreeable odour, boiling at 210° (corr.) and having a sp. gr. 0·8333 at 0°/4°, or 0·8213 at 16°/4°, and n_D 1·458 at 16°.

1-*Methyl*-4-sec.-*octyl*-4-cyclo*hexanol* is a colourless liquid with an agreeable odour, which boils at 150° under 8 mm. pressure and has a sp. gr. 0·8543 at 0°/4°.

4-*Phenyl*-1-*methyl*-4-cyclo*hexanol* forms brilliant prisms with an aromatic odour, which melt at 64° and boil at 145° under 6 mm.

pressure, the *phenylcarbamate* forms beautiful, elongated prisms melting at 135°, and the corresponding 4-*phenyl*-1-*methyl*cyclo*hexene* is a colourless liquid which boils at 147° under 23 mm. pressure, has a sp. gr. 0·9846 at 0°/4° or 0·9716 at 14°/4°, and n_D 1·555 at 14°.

4-*Benzyl*-1-*methyl*-4-cyclo*hexanol* is a liquid with an aromatic odour, which boils at 159° under 6 mm. pressure. The *phenylcarbamate* crystallises in brilliant needles which melt at 135°. 4-*Benzyl*-1-*methyl*cyclo*hexene*, $C_{14}H_{18}$, is a liquid with an agreeable odour, boils at 160° under 30 mm. pressure, has a sp. gr. 0·9687 at 0°/4° or 0·9567 at 16°/4°, and n_D 1·542 at 16°. M. A. W.

Nitrosophenol or Quinoneoxime. C. H. Sluiter (*Rec. Trav. chim.*, 1906, **25**, 8—11).—The synthesis of nitrosophenol by Goldschmidt (Abstr., 1884, 735) and that by Baeyer (*Ber.*, 1873, **6**, 963), both accomplished in ionising media, support the common view that free nitrosophenol has the quinoneoxime constitution. Bridge's synthesis (Abstr., 1894, i, 25), accomplished in dry ether, supports the view that it exists in the free state as a true nitroso-compound, and further evidence of this is afforded by O. Fischer and Hepp's preparation (Abstr., 1887, 1114) of nitrosoaniline from nitrosophenol in a dry condition in which ionisation could not occur. The fact that pure nitrosophenol is nearly white and that its solutions in non-ionising solvents are pale yellow, whilst those in ionising solvents are green, and that the colours of the hydrated salts are green and those of the anhydrous salts red (Farmer and Hantzsch, Abstr., 1900, i, 103), supports the author's view that in the free state nitrosophenol is a true nitroso-compound and that the salts have the oximino-structure.

Determination of the molecular weight of nitrosophenol, dissolved in benzene, by the ebullioscopic method showed that 50 per cent. of the substance was in the bimolecular condition, whereas in ether it appears to exist wholly in the unimolecular state. T. A. H.

***o*-Phenolsulphonates.** A. Vial (*Bull. Soc. chim.*, 1906, [iii], **35**, 159—165).—*Strontium*, *calcium*, lead, *silver*, *cadmium*, copper, *ferrous*, *aluminium*, *chromium*, *nickel*, *cobalt*, *manganese*, *magnesium*, sodium, potassium, *ammonium*, and *lithium* *o*-phenolsulphonates were prepared either by neutralising the acid with the carbonate of the appropriate metal or by double decomposition between barium *o*-phenolsulphonate and the appropriate metallic sulphate. The salts are all soluble in water, some of them also in alcohol, and all are insoluble in chloroform or benzene. The individual salts are described in detail in the original and in most cases crystallographic measurements are given.

T. A. H.

Oxidation by Fusion. Carl Graebe and Hermann Kraft (*Ber.*, 1906, **39**, 794—802).—A number of substances has been oxidised by addition of lead peroxide during fusion with sodium or potassium hydroxide at 200—220° or at 250—260°. Oxidation takes place more easily in this way, and gives better yields and purer products, than by fusion with the alkali hydroxide alone. The cresols yield the corresponding hydroxybenzoic acids, the toluic acids the corresponding phthalic acids. Phthalic anhydride, as also *o*-toluic acid, yields a small amount of an *acid* which melts at 270—280° and forms green, fluorescent solutions in aqueous alkali hydroxides.

Thymol remains almost unchanged at 210—220°, but at 250—260° is partially converted into a resin, the remainder undergoing complete oxidation. Eugenol yields *iso*eugenol, but is in part completely burnt or resinified.

1 : 3 : 4-Xylenol is oxidised to 4-hydroxy*iso*phthalic acid together with traces of 4-hydroxy-3-toluic acid. 2-Hydroxy*iso*phthalic acid is obtained by oxidation of *o*-cresotic acid; when treated with methyl sulphate in aqueous alkaline solution, it forms 2-methoxy*iso*phthalic acid, and, when boiled with methyl alcoholic hydrochloric acid, yields the *dimethyl* ester, $OH\cdot C_6H_3(CO_2Me)_2$, melting at 72°.

The oxidation of *p*-toluenesulphonic acid leads to the formation of benzoic and *p*-hydroxybenzoic acids; the oxidation of phenol to the formation of small amounts of salicylic acid, the phenol being regained mostly unchanged.

o-Phenylbenzoic acid is obtained by the oxidation of fluorene, protocatechuic acid in a yield of 43·6 of the theoretical by the oxidation of quinic acid, a part of which is completely oxidised. G. Y.

Preparation of 4-Chloro-2-nitroanisole. K. Oehler (D.R.-P. 161664. Compare Abstr., 1903, i, 478).—In the action of chlorine on *o*-nitroanisole in presence of a chlorine carrier, the hydrogen chloride produced causes the hydrolysis of a large part of the ether. Perfect chlorination is, however, obtained in presence of an organic acid. Thus the addition of 15 per cent. of formic acid allows the chlorination to take place at 50—60° without any loss by hydrolysis. Acetic or chloroacetic acid may also be used. C. H. D.

Structure of the Dinitroanisoles. H. Vermeulen (*Rec. Trav. chim.*, 1906, **25**, 12—31).—In view of the unexpected results obtained by Holleman in his investigation of the nitration of the nitroanisoles (Abstr., 1903, i, 623), the author has investigated the reduction and methylation products of the dinitroanisoles. The results confirm the constitutions assigned by Henriques (Abstr., 1883, 327) to the latter substances.

It was found possible to prepare the 2 : 3- and 3 : 4-dinitroanisoles by shaking aqueous solutions of the sodium derivatives of the corresponding dinitrophenols with excess of methyl sulphate. 3 : 6-Dinitroanisole was obtained by warming a dry mixture of the potassium derivative of 3 : 6-dinitrophenol with methyl sulphate at 100°. Veratrole was prepared by adding gradually and with continuous agitation an *N*/5 solution of sodium hydroxide to a mixture of catechol and methyl sulphate previously melted together at 100°. This method of methylation is also applicable to the other dihydroxybenzenes.

2-*Nitro*-1 : 3-*dimethoxybenzene*, prepared by shaking the sodium derivative of 2-nitroresorcinol, dissolved in water, with a slight excess of methyl sulphate, crystallises from alcohol in long, colourless needles, melts at 130°, solidifies at 129·7° (corr.), has a sp. gr. 1·1520 at 132°, and is soluble in the usual organic solvents, but insoluble in water and light petroleum.

5-*Nitro*-1 : 3-*dimethoxybenzene*, similarly prepared from 5-nitro-3-methoxyphenol, crystallises from ethyl acetate in transparent, yellow needles, melts at 89°, solidifies at 87·6°, has a sp. gr. 1·169 at 132°, and is insoluble in water and light petroleum. The 3 : 6- and 3 : 4-dinitroanisoles yield the same 4-nitro-1 : 3-dimethoxybenzene when treated with sodium methoxide in methyl alcohol, and 2 : 3-dinitroanisole, under similar conditions, produces 3-nitro-1 : 2-dimethoxybenzene, but the dinitroanisoles having the nitro-groups in the meta-position relatively to each other do not suffer the replacement of one nitro-group by a methoxyl group under these conditions.

Ammonium sulphide does not reduce the 2 : 3- and 2 : 6-dinitroanisoles or those in which the two nitro-groups occupy the ortho-position relatively to each other. In the 2 : 4- and 3 : 6-dinitroanisoles, the NO_2 group nearer to the methoxyl group is reduced by this reagent.

The solidifying points and specific gravities of the various nitromethoxyanilines and nitrodimethoxybenzenes prepared were determined and are tabulated in the original. T. A. H.

Preparation of *p*-Iodoxyanisole and *p*-Iodoxyphenetole. ARTHUR LIEBRECHT (D.R.-P. 161725).—The method employed for the preparation of *o*-iodoxyanisole (Jannasch and Hinterskirch, Abstr., 1898, i, 575) is not applicable to *m*-iodoanisole.

p-Iodoanisole is acted on in aqueous suspension by chlorine or by hypochlorous acid, the final product being *p*-iodoxyanisole. The *iododichloride* forms golden-yellow crystals and undergoes spontaneous change, the chlorine migrating into the ring. The *iodoso*-compound forms white crystals and decomposes spontaneously. p-*Iodoxyanisole* crystallises from 50 per cent. acetic acid in silvery-white leaflets, explodes at 225°, and is insoluble in alcohol or ether, but dissolves in hot water. p-*Iodoxyphenetole* is similar, and also explodes at 225°. Both compounds have strong oxidising and antiseptic properties.

C. H. D.

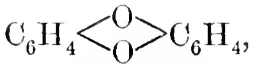
Action of Disulphides on Organo-magnesium Haloids. Synthesis of Mixed Sulphides. HENRI WUYTS (*Bull. Soc. chim.*, 1906, [iii], **35**, 166—169. Compare Abstr., 1903, i, 686, and Taboury, *ibid.*, 748).—When phenyl disulphide reacts with magnesium ethyl bromide and the reaction product is decomposed with water, phenyl ethyl sulphide and thiophenol are formed. Phenyl α-naphthyl sulphide, prepared similarly from phenyl disulphide and magnesium α-naphthyl bromide, boils at 255—256° under 43 mm. pressure and has a sp. gr. 1·167 at 15°/4° (compare Krafft and Bourgeois, Abstr., 1891, 76). *Ethyl* iso*butyl sulphide*, resulting similarly, together with ethyl mercaptan, *iso*butyl chloride, and *iso*butyl alcohol, by the interaction of ethyl disulphide with magnesium *iso*butyl chloride, is a mobile liquid of pungent odour, boils at 132—134° (corr.), has a sp. gr. 0·8337 at 15°/4°, and n_D 1·44677. T. A. H.

Preparation of α-Methyl-β-naphthol. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 161450).—Di-β-hydroxy-α-naphthylmethane, prepared from formaldehyde and β-naphthol, undergoes a remarkable change when reduced with zinc dust in boiling sodium hydroxide solution, being converted into α-methyl-β-naphthol and β-naphthol, $CH_2(C_{10}H_6\cdot OH)_2 + H_2 = C_{10}H_6Me\cdot OH + C_{10}H_7\cdot OH$ (compare Boehm, Abstr., 1902, i, 37). The products are separated by the addition of formaldehyde, precipitation with hydrochloric acid, and crystallisation from water.

α-Methyl-β-naphthol crystallises in needles, melts at 112°, and dissolves in alcohol, ether, or benzene. The *benzoyl* derivative crystallises from alcohol in long needles and melts at 117°; the *ethyl ether* melts at 52°. C. H. D.

Diphenylene Dioxide. FRITZ ULLMANN and ALBERT STEIN (*Ber.*, 1906, **39**, 622—625. Compare Ullmann, Sponagel, and Stein, Abstr., 1905, i, 644).—*o*-Methoxydiphenyl ether is prepared by gradually heating a mixture of guaiacol, bromobenzene, potassium hydroxide, and copper powder at 220—230°, or by heating phenol with *o*-bromoanisole, potassium hydroxide, and copper powder at 190—215° for four hours. It crystallises from light petroleum in white needles, melts at 78°, boils at 228°, and volatilises slowly in a current of steam. When boiled with aluminium chloride in benzene solution in a reflux apparatus, it yields *o-hydroxydiphenyl ether*, $OH\cdot C_6H_4\cdot OPh$, which crystallises from light petroleum in colourless plates, melts at 107°, is only sparingly soluble in boiling water, but readily so in boiling alcohol or ether, and is volatile with steam; on addition of ferric chloride, the aqueous solution becomes red and opaque.

2 : 2′-*Dimethoxydiphenyl ether*, $O(C_6H_4\cdot OMe)_2$, is prepared by heating a mixture of guaiacol, *o*-bromoanisole, potassium hydroxide, and copper powder at 180—190°; it crystallises in white leaflets, melts at 78°, boils at 330—331°, and when boiled with aluminium chloride and benzene forms 2 : 2′-*dihydroxydiphenyl ether*, $O(C_6H_4\cdot OH)_2$. This crystallises from light petroleum in large, almost colourless plates, or from water in long needles, melts at 121°, and gives a blue coloration with ferric chloride.



Diphenylene dioxide, $C_6H_4{<}\overset{O}{\underset{O}{}}{>}C_6H_4$, is formed by heating 2 : 2′-dihydroxydiphenyl ether or 2 : 2′-dimethoxydiphenyl ether with hydrobromic acid of sp. gr. 1·49 at 180—190°; it crystallises in long, colourless needles, resembling asbestos, and melts at 119°.

Di-2 : 3-naphthylene dioxide crystallises in colourless leaflets, melts at 326°, and dissolves in pyridine or toluene, forming a solution with blue fluorescence. G. Y.

Relations between the Constitution and the Stability of the Condensation Products of Organic Bases with Substituted Hydroxybenzyl Bromides. KARL AUWERS (*Annalen*, 1906, **344**, 93—141. Compare Abstr., 1896, i, 149; 1902, i, 146).—A summary of results previously obtained and an introduction to the four papers following.

The complete work embraces the preparation of seventeen substituted hydroxybenzyl bromides and the study of their condensation products with ammonia, methyl-, ethyl-, benzyl-, diethyl-, and diamylamines, aniline, methylaniline, α- and β-naphthylamines, and piperidine, and of the quaternary salts formed with pyridine and quinoline. The condensation products are formed by the interaction of the amines with ψ-phenolic benzyl bromides in cold, with phenolic benzyl bromides in hot, ethereal or benzene solution. The stability of the condensation products towards cold and hot dilute sodium hydroxide, cold and hot anhydrous acetic acid, boiling acetic anhydride, and prolonged heating on the water-bath, has been investigated, and found to depend on the nature of the amine as well as on that of the phenol constituent. The results are given in a series of tables. G. Y.

Condensation Products of Organic Bases with Phenols and ψ-Phenols of the Cresol Series. Karl Auwers and O. Schröter (*Annalen*, 1906, **344**, 141—170. See preceding abstract).—3 : 5-Dibromo-2-hydroxybenzyl bromide (Auwers and Büttner, Abstr., 1899, i, 36) is prepared best by heating *o*-cresol with bromine at 115—120°. The piperidine derivative remains unchanged when boiled with 10 per cent. sodium hydroxide or glacial acetic acid for one hour, or when heated alone on the water-bath, but when boiled with acetic anhydride yields piperidine and dibromosaligenin diacetate, melting at 70—71°. The *methylamine* derivative, $NMe(CH_2\cdot C_6H_2Br_2\cdot OH)_2$, is not decomposed when heated at 100° or when boiled with dilute sodium hydroxide or glacial acetic acid, and yields only a small amount of methylamine when boiled with acetic anhydride.

The *benzylamine* derivative, $CH_2Ph\cdot NH\cdot CH_2\cdot C_6H_2Br_2\cdot OH$, crystallises from methyl alcohol in silvery needles, melts at 129—130°, is stable to boiling dilute sodium hydroxide, but yields a small amount of benzylamine when boiled with glacial acetic acid, and is decomposed completely by boiling acetic anhydride.

The *diamylamine* derivative, $N(C_5H_{11})_2\cdot CH_2\cdot C_6H_2Br_2\cdot OH$, is isolated in the form of its *hydrochloride*, $C_{17}H_{27}ONBr_2,HCl$; it is decomposed by 5 per cent. aqueous sodium hydroxide, slightly at the laboratory temperature, to a greater extent when heated, and when boiled with glacial acetic acid or acetic anhydride yields dibromosaligenin mono- and di-acetate respectively. Dibromosaligenin monoacetate, melting at 110—112°, is soluble in dilute sodium hydroxide and remains unchanged when boiled with methyl alcohol or a mixture of methyl alcohol or water and acetone.

*Tetrabromo-*o*-hydroxybenzyl bromide*, $OH\cdot C_6Br_4\cdot CH_2Br$, is prepared by brominating *o*-cresol at the laboratory temperature and heating the product with bromine in a sealed tube at 100°; it crystallises from glacial acetic acid and melts at 156°. The *methylamine* derivative, $NMe(CH_2\cdot C_6Br_4\cdot OH)_2$, melts at 205—207°, and when boiled with acetic anhydride forms a *diacetyl* derivative, $NMe(CH_2\cdot C_6Br_4\cdot OAc)_2$, which melts at 145—150°. The *piperidine* derivative,

$$C_5H_{10}N\cdot CH_2\cdot C_6Br_4\cdot OH,$$

forms a yellow powder, melts at 106—108°, and when boiled with acetic anhydride yields *tetrabromosaligenin diacetate*, $C_7H_2Br_4(OAc)_2$, which melts at 138—139°. The *benzylamine* derivative,

$$CH_2Ph\cdot NH\cdot CH_2\cdot C_6Br_4\cdot OH,$$

crystallises in leaflets, melts at 170—171°, and is decomposed only slightly by boiling 5 per cent. sodium hydroxide or by cold glacial acetic acid, but when boiled with glacial acetic acid yields *tetrabromosaligenin acetate*, $OH\cdot C_6Br_4\cdot CH_2\cdot OAc$, which melts at 133° and remains unchanged when boiled with methyl alcohol or aqueous acetone. When boiled with acetic anhydride, the benzylamine compound forms the *acetyl* derivative, $CH_2Ph\cdot NAc\cdot C_6Br_4\cdot OH$, which crystallises in glistening prisms and melts at 150°. The *diamylamine* derivative,

$$N(C_5H_{11})_2\cdot CH_2\cdot C_6Br_4\cdot OH,$$

is an oil which forms a solid *hydrochloride*, $C_{17}H_{23}ONBr_4,HCl$; it is decomposed only slightly by boiling dilute sodium hydroxide or cold glacial acetic acid, but yields tetrabromosaligenin monoacetate when boiled with glacial acetic acid, or the diacetate when boiled with acetic anhydride.

Tetrabromo-m-*hydroxybenzyl bromide*, $OH\cdot C_6Br_4\cdot CH_2Br$, melting at 137° (Auwers and Anselmino, Abstr., 1900, i, 159), is prepared by heating tetrabromo-*m*-cresol with bromine in a sealed tube at 100°. The *piperidine* derivative, $C_{12}H_{13}ONBr_4$, crystallises from benzene in slender, white needles, melts at 193°, yields only traces of piperidine when boiled with dilute sodium hydroxide or glacial acetic acid, and is converted by boiling acetic anhydride into the *acetyl* derivative, $C_5H_{10}N\cdot CH_2\cdot C_6Br_4\cdot OAc$, which melts at 129—130°. The *methylamine* derivative, $NMe(CH_2\cdot C_6Br_4\cdot OH)_2$, resembles the piperidine derivative, but could not be obtained in a state of purity. The *diamylamine* derivative, $N(C_5H_{11})_2\cdot CH_2\cdot C_6Br_4\cdot OH$, crystallises in matted, slender needles, melts at 167—168°, is only slightly decomposed by boiling dilute sodium hydroxide or glacial acetic acid, and when boiled with acetic anhydride yields the *acetate*, $N(C_5H_{11})_2\cdot CH_2\cdot C_6Br_4\cdot OAc$, which is hydrolysed by boiling alcoholic sodium hydroxide.

The *methylamine* derivative, $NMe(CH_2\cdot C_6H_2Br_2\cdot OH)_2$, formed from 3 : 5-dibromo-4-hydroxybenzyl bromide and methylamine, is obtained as a crystalline powder, melts at 180°, is decomposed by boiling glacial acetic acid with formation of methylamine and 3 : 5-dibromo-4-hydroxybenzyl acetate, melting at 115°, and when boiled with acetic anhydride yields the diacetate, melting at 68° (Auwers and Daecke, Abstr., 1900, i, 164). The *piperidine* derivative,

$$C_5H_{10}N\cdot CH_2\cdot C_6H_2Br_2\cdot OH,$$

forms a yellow, micro-crystalline powder, melts at 183°, and, in its behaviour to acetic acid and acetic anhydride, resembles the methylamine derivative. The *benzylamine* derivative,

$$CH_2Ph\cdot NH\cdot CH_2\cdot C_6H_2Br_2\cdot OH,$$

is isolated in the form of its *hydrochloride*, $C_{14}H_{14}ONClBr_2$; it yields a small amount of benzylamine when boiled with dilute sodium hydroxide, is completely decomposed by boiling glacial acetic acid containing sodium acetate, with formation of benzylamine and 3 : 5 : 3′ : 5′-tetrabromo-4 : 4′-dihydroxydiphenylmethane, and when boiled with acetic anhydride yields a resinous, nitrogenous *product*, which is insoluble in aqueous alkali hydroxides. The *diamylamine* derivative, $N(C_5H_{11})_2\cdot CH_2\cdot C_6H_2Br_2\cdot OH$, is obtained as a glutinous, friable mass, which melts at 70—97° and decomposes when recrystallised or when heated on the water-bath; it is decomposed to the extent of about 25 per cent. when boiled with dilute sodium hydroxide, or completely with formation of 3 : 5 : 3′ : 5′-tetrabromo-4 : 4′-dihydroxydiphenylmethane, or of its acetyl derivative respectively, when boiled with glacial acetic acid or acetic anhydride.

The *methylamine* derivative, NMe(CH$_2$·C$_6$Br$_4$·OH)$_2$, prepared from tetrabromo-*p*-hydroxybenzyl bromide, crystallises in slender, white needles, melts at 215°, and is decomposed by boiling glacial acetic acid with formation of the monoacetyl or by boiling acetic anhydride with formation of the diacetyl derivative of tetrabromo-*p*-hydroxybenzyl alcohol (Zincke and Wiederhold, Abstr., 1902, i, 285). The *piperidine* derivative, C$_5$H$_{10}$N·CH$_2$·C$_6$Br$_4$·OH, crystallises in white scales, melts at about 185°, and behaves towards acetic acid and acetic anhydride in the same way as the methylamine derivative. The *benzylamine* derivative, CH$_2$Ph·NH·CH$_2$·C$_6$Br$_4$·OH, melts at 163°, yields only traces of benzylamine when boiled with dilute sodium hydroxide, and is converted by boiling glacial acetic acid into octabromo-4 : 4′-dihydroxydiphenylmethane, melting at 276—277° (Zincke and Böttcher, this vol., i, 166); its *diacetyl* derivative, CH$_2$Ph·NAc·CH$_2$·C$_6$Br$_4$·OAc, formed by boiling the benzylamine compound with acetic anhydride, crystallises in stout needles, melts at 146—147°, and when boiled with alcoholic sodium hydroxide is hydrolysed to the *monoacetyl* derivative,

CH$_2$Ph·NAc·CH$_2$·C$_6$Br$_4$·OH.

The *diamylamine* derivative, N(C$_5$H$_{11}$)$_2$·CH$_2$·C$_6$Br$_4$·OH, is obtained as a resin, decomposes slowly when heated on the water-bath, and yields diamylamine and octabromodi-*p*-hydroxyphenylmethane when boiled with dilute sodium hydroxide or glacial acetic acid. The base, when boiled with acetic anhydride, yields *octabromodi-*p*-acetoxyphenylmethane*, C$_{17}$H$_8$O$_4$Br$_8$, melting at 276—277°.

With the exception of the diamylamine derivatives from 3:5-dibromo- and tetrabromo-hydroxybenzyl bromides, the bases described in this paper remain unchanged when heated on the water-bath for one hour.

G. Y.

Condensation Products of Organic Bases with Phenols and ψ-Phenols of the Xylenol and Hemimellithenol Series. KARL AUWERS, C. KIPKE, A. SCHRENK, and O. SCHRÖTER (*Annalen*, 1906, **344**, 171—193. Compare preceding abstract).—3 : 5-*Dibromo-1 : 2 : 4-xylenol*, OH·C$_6$HMe$_2$Br$_2$, is prepared by the action of bromine on 1 : 2 : 4-xylenol in concentrated glacial acetic acid solution; it crystallises in slender, white needles, melts at 39—40°, boils at about 300°, and is readily soluble in organic solvents. The *benzoate*, C$_{15}$H$_{12}$O$_2$Br$_2$, crystallises in slender needles and melts at 125—126°. ω : 3 : 5-*Tribromo-1 : 2 : 4-xylenol*, C$_8$H$_7$OBr$_3$, is formed by adding bromine to 3 : 5-dibromo-1 : 2 : 4-xylenol heated to 120—130°; it crystallises in slender needles and small, nodular aggregates, melts at 90—97°, and is insoluble in aqueous alkali hydroxides.

ω : 3 : 5 : 6-Tetrabromo-1 : 2 : 4-xylenol, melting at 173° (Auwers and Erggelet, Abstr., 1900, i, 97), is prepared best by heating tribromoxylenol with half its weight of bromine in a sealed tube at 100°. The *piperidine* derivative, C$_5$H$_{10}$N·CH$_2$·C$_6$MeBr$_3$·OH, crystallises in stout, nacreous leaflets, melts at 159·5—160°, is readily soluble in glacial acetic acid, and is hydrolysed only partially by boiling dilute sodium hydroxide, but almost completely by boiling glacial acetic acid; when boiled with acetic anhydride, it yields the diacetyl derivative of

3 : 5 : 6-tribromo-ω : 4-dihydroxy-1 : 2-xylene, melting at 135—137° (Auwers and Erggelet, *loc. cit.*).

The *methylamine* derivative, $NMe(CH_2\cdot C_6MeBr_3\cdot OH)_2$, formed from ω : 2 : 5 : 6-tetrabromo-1 : 3 : 4 xylenol (Auwers and Campenhausen, Abstr., 1896, i, 424), softens at 155°, melts at 161°, is readily soluble in benzene, or moderately so in ethyl acetate, chloroform, or alcohol, and when boiled with glacial acetic acid yields methylamine and the monoacetyl derivative of tribromo-4-hydroxy-1 : 3-xylyl alcohol, melting at 153—154° (Auwers and Ziegler, Abstr., 1897, i, 33). The base is decomposed also by boiling acetic anhydride, with formation of 2 : 5 : 6-*tribromo-ω* : 4-*diacetoxy*-1 : 3-*xylene*, $OAc\cdot C_6MeBr_3\cdot CH_2\cdot OAc$, which crystallises in needles and melts at 136—136·5°. The piperidine derivative, $C_5H_{10}N\cdot CH_2\cdot C_6MeBr_3\cdot OH$, which melts at 157° (Auwers and Ziegler, *loc. cit.*), is decomposed in the same way as the methylamine derivative by acetic acid and acetic anhydride. The *benzylamine* derivative, $CH_2Ph\cdot NH\cdot CH_2\cdot C_6MeBr_3\cdot OH$, crystallises in short, glistening prisms, melts at 138°, and when boiled with glacial acetic acid yields the monoacetate of tribromo-4-hydroxy-1 : 3-xylyl alcohol. The *diacetyl* derivative, $CH_2Ph\cdot NAc\cdot CH_2\cdot C_6MeBr_3\cdot OAc$, formed by boiling the base with acetic anhydride, crystallises in microscopic leaflets and melts at 118—120°. The *diamylamine* derivative,

$$N(C_5H_{11})_2\cdot CH_2\cdot C_6MeBr_3\cdot OH,$$

crystallises in matted, small needles, melts at 99—100°, does not give the potassium test for nitrogen, decomposes slightly on prolonged heating on the water-bath, and yields only small quantities of diamylamine when boiled with aqueous sodium hydroxide; when boiled with acetic acid and with acetic anhydride, the base yields the mono- and di-acetates of tribromo-4-hydroxy-1 : 3-xylyl alcohol respectively. When boiled with methyl alcohol, the monoacetate is converted into the monomethyl ether, $OH\cdot C_6MeBr_3\cdot CH_2\cdot OMe$.

ω : 2 : 5 : 6-Tetrabromo-3-hydroxy-*p*-xylene (Auwers and Anselmino, Abstr., 1900, i, 159; Auwers and Ebner, *ibid*, 161) is prepared best by the action of an excess of bromine and water on tetrabromo-ψ-cumenol. The *methylamine* derivative, $NMe(CH_2\cdot C_6MeBr_3\cdot OH)_2$, is obtained as a white, amorphous powder, melts at 151—152°, and when heated alone on the water-bath, or digested at the laboratory temperature for eighteen hours, or boiled for one hour with aqueous sodium hydroxide, yields hexabromodi-*m*-hydroxydi-*p*-tolylmethane; when boiled with acetic anhydride, the base forms the *diacetate*,

$$NMe(CH_2\cdot C_6MeBr_3\cdot OAc)_2,$$

which crystallises in thin, colourless, rhombic leaflets and melts at 132—133°. The *piperidine* derivative, $C_5H_{10}N\cdot CH_2\cdot C_6MeBr_3\cdot OH$, crystallises in colourless plates, melts at 116—117°, and is decomposed by boiling dilute sodium hydroxide in one hour to the extent of 22·3—24·8 per cent., yielding a *product* which melts at a high temperature and is soluble in aqueous alkali hydroxides; when boiled with acetic anhydride, the base forms the *acetate*, $C_{15}H_{18}O_2NBr_3$, which crystallises in slender, white needles and melts at 92—94°. The *diamylamine* derivative, $N(C_5H_{11})_2\cdot CH_2\cdot C_6MeBr_3\cdot OH$, crystallises in glistening, white needles, melts at 81—81·5°, and when boiled with dilute sodium hydroxide or glacial acetic acid is rapidly converted into hexabromodi-*m*-hydroxydi-*p*-tolylmethane, the *acetate* of which is formed by boiling the base with acetic anhydride; it melts at 260° and is insoluble in dilute alkali hydroxides.

*Hexabromodi-*m*-hydroxydi-*p*-tolylmethane*, $CH_2(C_6MeBr_3\cdot OH)_2$, crystallises from a mixture of benzene and toluene in small, white scales, melts at 251°, and is moderately soluble in alcohol or glacial acetic acid.

2 : 5 : 6-*Tribromo-3-hydroxy-*p*-xylyl acetate*, $OH\cdot C_6MeBr_3\cdot CH_2\cdot OAc$, formed by boiling the tetrabromo-compound with sodium acetate in acetic acid solution, crystallises in slender, light yellow prisms, melts at 132—134°, and remains unchanged when boiled with methyl alcohol or aqueous acetone, or when dissolved in dilute sodium hydroxide, and is quickly reprecipitated by adding an acid.

*Dibromo-*p*-hydroxyhemimellithyl bromide*,

$$OH\cdot C{<}\begin{array}{c}CBr\cdot CMe\\ CBr{:}CMe\end{array}{>}C\cdot CH_2Br,$$

melts at 140—142°. The *piperidine* derivative,

$$OH\cdot C_6Me_2Br_2\cdot CH_2\cdot C_5H_{10}N,$$

crystallises in sheaves of long needles, melts at 110°, decomposes gradually with evolution of piperidine when heated on the water-bath, and is decomposed to only a slight extent by cold glacial acetic acid or aqueous sodium hydroxide, but completely with formation of tetrabromodihydroxytetramethyldiphenylmethane when boiled in alkaline solution. The *diamylamine* derivative,

$$OH\cdot C_6Me_2Br_2\cdot CH_2\cdot N(C_5H_{11})_2,$$

melts and decomposes at 81° and is decomposed rapidly by boiling aqueous sodium hydroxide.

3 : 5 : 3′ : 5′-*Tetrabromo-*4 : 4′*-dihydroxy-*2 : 6 : 2′ : 6′*-tetramethyldiphenylmethane*, $CH_2(C_6Me_2Br_2\cdot OH)_2$, crystallises in matted, slender needles and melts at 246°. With the exception of the diamylamine derivative of 2 : 5 : 6-tribromo-4-hydroxy-*m*-xylyl bromide, and the methylamine derivative of 2 : 5 : 6-tribromo-3-hydroxy-*p*-xylyl bromide, and the piperidine and diamylamine derivatives of dibromo-*p*-hydroxyhemimellithyl bromide, the bases described above remain unchanged when heated on the water-bath for one hour. G. Y.

Condensation Products of Organic Bases with Phenols and ψ-Phenols of the ψ-Cumenol Series. KARL AUWERS and C. KIPKE (*Annalen*, 1906, **344**, 194—226. Compare preceding abstracts).—3-Bromo-2-hydroxy-ψ-cumyl bromide, melting at 66—67° (Auwers and Rovaart, Abstr., 1899, i, 34), is formed by bromination of *o*-hydroxy-ψ-cumyl alcohol (Auwers and Anselmino, Abstr., 1902, i, 214) in ether-chloroform solution. The *methylamine* derivative,

$$NMe(CH_2\cdot C_6HMe_2Br\cdot OH)_2,$$

crystallises in glistening, flat plates, melts at 116—117°, and when boiled with acetic anhydride is partially decomposed with formation of methylamine. The *piperidine* derivative, $C_5H_{10}N\cdot CH_2\cdot C_6HMe_2Br\cdot OH$, crystallises in long, transparent needles, melts at 87—88°, and when boiled with acetic anhydride yields the *diacetate* of 3-bromo-2-hydroxy-ψ-cumyl alcohol, $OAc\cdot C_6HMe_2Br\cdot CH_2\cdot OAc$, which is formed also by boiling the bromide with sodium acetate and acetic anhydride. It crystallises in slender needles and melts at 51—52°. The *benzylamine* derivative, $CH_2Ph\cdot N(CH_2\cdot C_6HMe_2Br\cdot OH)_2$, crystallises in slender needles, melts at 147—148°, and is decomposed by boiling acetic anhydride in the same manner as, but more completely than, the methylamine derivative. The *diamylamine* derivative,

$$N(C_5H_{11})_2\cdot CH_2\cdot C_6HMe_2Br\cdot OH,$$

is an oil which is hydrolysed with formation of diamylamine by glacial acetic acid at the laboratory temperature, and when boiled with acetic anhydride yields the diacetate of 3-bromo-2-hydroxy-ψ-cumyl alcohol.

The *piperidine* derivative,  $CMe{<}\begin{matrix}C(OH)\cdot CBr\\ CBr{=}CMe\end{matrix}{>}C\cdot CH_2\cdot C_5NH_{10}$, formed from 3 : 6-dibromo-5-hydroxy-ψ-cumyl bromide, melting at 128° (Auwers and Maas, Abstr., 1900, i, 162), crystallises in long, flat needles, melts at 68—69°, is readily soluble in organic solvents, and remains unchanged when boiled with 5 per cent. aqueous sodium hydroxide.

The *methylamine* derivative, $NMe(CH_2\cdot C_6HMe_2Br\cdot OH)_2$, formed from 3-bromo-4-hydroxy-ψ-cumyl bromide, melting at 81° (Auwers and Ercklentz, Abstr., 1899, i, 35), crystallises in plates or stellate aggregates of needles, melts at 150—151°, when boiled with dilute sodium hydroxide yields 3 : 3′-dibromo-4 : 4′-dihydroxy-2 : 5 : 2′ : 5′-tetramethyldiphenylmethane, melting at 151—153° (Auwers, Abstr., 1903, i, 622), and is converted by boiling with glacial acetic acid into the monoacetate, with acetic anhydride into the diacetate of bromo-*p*-hydroxy-ψ-cumyl alcohol (Auwers and Ercklentz, *loc. cit.*). 3-Bromo-4-hydroxy-ψ-cumylpiperidine (Auwers and Ercklentz, *loc cit.*) yields the diphenylmethane derivative when heated on the water-bath or when boiled with aqueous sodium hydroxide, and when boiled with glacial acetic acid or acetic anhydride yields the mono- or di-acetate, respectively, of bromo-*p*-hydroxy-ψ-cumyl alcohol. The *benzylamine* derivative, $CH_2Ph\cdot N(CH_2\cdot C_6HMe_2Br\cdot OH)_2$, crystallises in stellate aggregates of needles, melts at 123—133°, and when boiled with dilute sodium hydroxide, glacial acetic acid, and acetic anhydride yields the diphenylmethane and the mono- and di-acetates respectively of the ψ-cumyl alcohol. The *diamylamine* derivative,

$$N(C_5H_{11})_2\cdot CH_2\cdot C_6HMe_2Br\cdot OH,$$

is isolated in the form of its hydrochloride, $C_{19}H_{32}ONBr,HCl$; the base decomposes and forms the diphenylmethane derivative when heated on the water-bath or boiled with dilute sodium hydroxide, or less completely when shaken with cold aqueous sodium hydroxide; it is decomposed by boiling glacial acetic acid, or, with formation of the diacetate of the ψ-cumyl alcohol, by boiling acetic anhydride.

The following bases are prepared from 3 : 6-dibromo-4-hydroxy-ψ-cumyl bromide (Auwers and Marwedel, Abstr., 1896, i, 149). The ammonia derivative, $N(CH_2\cdot C_6Me_2Br_2\cdot OH)_3$ (Auwers and Hof, Abstr., 1896, i, 421), is partially decomposed by boiling dilute sodium hydroxide with formation of the diphenylmethane derivative, $CH_2(C_6Me_2Br\cdot OH)_2$, melting at 232°, and when boiled with glacial acetic acid forms a solution which, on cooling, deposits the diphenylmethane derivative, but if diluted with water whilst hot yields the monoacetate of 3 : 6-dibromo-4-hydroxy-ψ-cumyl alcohol, melting at

112—115°; when boiled with acetic anhydride, the tertiary base is converted into the diacetate of dibromo-4-hydroxy-ψ-cumyl alcohol, together with a small quantity of a nitrogenous *product*. The methylamine derivative (Auwers and Hof, *loc. cit.*) is decomposed by boiling 10 per cent. sodium hydroxide with formation of the diphenylmethane derivative melting at 232°, but remains almost unchanged when boiled with 2½ per cent. aqueous sodium hydroxide; it is decomposed by glacial acetic acid only slowly at the laboratory temperature, quickly when boiled, with formation of the monoacetate of the ψ-cumyl alcohol, or by boiling acetic anhydride, with formation of the diacetate of the ψ-cumyl alcohol. When boiled with acetic anhydride, the hydrobromide of the methylamine base yields 3 : 6-dibromo-4-acetoxy-ψ-cumyl bromide melting at 161°. The ethylamine derivative (Auwers and Hof, *loc. cit.*) is decomposed by aqueous sodium hydroxide, glacial acetic acid, and acetic anhydride in the same way and with formation of the same products as is the methylamine derivative; when boiled with absolute alcohol, the base yields ethylamine and 3 : 6-dibromo-4-hydroxy-ψ-cumyl ethyl ether, melting at 85—87°. The *benzylamine* derivative, $CH_2Ph\cdot N(CH_2\cdot C_6Me_2Br_2\cdot OH)_2$, crystallises in broad needles, melts at 183—184°, and when boiled with 10 per cent. aqueous sodium hydroxide, glacial acetic acid, and acetic anhydride, yields benzylamine and the diphenylmethane derivative melting at 232°, and the mono- and di-acetate of dibromo-4-hydroxy-ψ-cumyl alcohol respectively. A second preparation of the base was much more stable towards cold glacial acetic acid or boiling dilute sodium hydroxide. The β-naphthylamine derivative,

$$NH(C_{10}H_7)\cdot CH_2\cdot C_6Me_2Br_2\cdot OH$$

(Auwers and Senter, Abstr., 1896, i, 423), remains unchanged when boiled with 5 per cent. aqueous sodium hydroxide; the action of boiling glacial acetic acid on the base leads to the formation of the *monoacetyl* derivative, $N(C_{10}H_7)Ac\cdot CH_2\cdot C_6Me_2Br_2\cdot OH$, which crystallises in strongly refracting, monoclinic prisms and melts at 226—227·5°. The *diacetyl* derivative, $N(C_{10}H_7)Ac\cdot CH_2\cdot C_6Me_2Br_2\cdot OAc$, formed by boiling the base with acetic anhydride, crystallises in small, white needles and melts at 148·5—151·5°. The *α-naphthylamine* derivative, $C_{19}H_{17}ONBr_2$, crystallises in small, glistening, slightly brown or violet needles, melts at 196—197°, and is slightly less stable than the β-naphthylamine derivative. The diethylamine derivative (Auwers and Hof, *loc. cit.*) yields diethylamine and the diphenylmethane derivative melting at 232° when heated on the water-bath or when boiled with 10 per cent. aqueous sodium hydroxide or with glacial acetic acid; the action of boiling acetic anhydride on the base leads to the formation of the diacetate of the ψ-cumyl alcohol, on the hydrobromide of the base, to the formation of the acetate of dibromo-4-hydroxy-ψ-cumyl bromide. The *diamylamine* derivative,

$$N(C_5H_{11})_2\cdot CH_2\cdot C_6Me_2Br_2\cdot OH,$$

melts at 43—45°, decomposes with formation of the diphenylmethane derivative when heated on the water-bath or when shaken with cold dilute sodium hydroxide or glacial acetic acid, and when boiled with glacial acetic acid yields the monoacetate, or with acetic anhydride the diacetate of dibromo-4-hydroxy-ψ-cumyl alcohol. The methylaniline derivative (Auwers and Senter, *loc. cit.*) is decomposed with formation of the diphenylmethane derivative, slowly at the laboratory temperature, quickly when boiled with sodium hydroxide; the action of glacial acetic acid on the base leads to the formation of mixtures of the unchanged base with the diphenylmethane derivative; when boiled with acetic anhydride, the base yields the diacetate of dibromo-4-hydroxy-ψ-cumyl alcohol. The piperidine derivative (Auwers and Marwedel, *loc. cit.*) is almost completely decomposed by boiling 10 per cent. aqueous sodium hydroxide with formation of piperidine and the diphenylmethane derivative; when boiled with glacial acetic acid, it yields the diacetate melting at 113—115°, together with a small quantity of the diphenylmethane derivative; the *acetyl* derivative,

$$C_5H_{10}N\cdot CH_2\cdot C_6Me_2Br_2\cdot OAc,$$

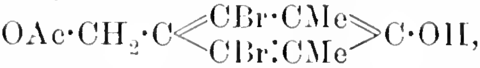
formed by boiling the base with acetic anhydride, crystallises in fern-like aggregates of needles and melts at 97°. The piperidine base yields the diphenylmethane derivative also when heated on the water-bath and when boiled with toluene or with alcohol. The quaternary bromide formed from 3 : 6-dibromo-4-hydroxy-ψ-cumyl bromide and pyridine (Auwers and Avery, Abstr., 1896, i, 150) is decomposed by boiling glacial acetic acid with formation of the monoacetate melting at 112—115°, or by boiling acetic anhydride with formation of the acetate of dibromo-4-hydroxy-ψ-cumyl bromide. The quaternary bromide formed with quinoline (Auwers and Senter, *loc. cit.*) is decomposed by boiling aqueous sodium hydroxide with formation of the diphenylmethane derivative or by glacial acetic acid or acetic anhydride in the same way as the pyridine bromide. The aniline derivative (Auwers and Marwedel, *loc. cit.*) is not decomposed by heating on the water-bath or by boiling with dilute sodium hydroxide; when boiled with glacial acetic acid, it forms the acetate melting at 224°, or, with acetic anhydride, the diacetate melting at 140° (Auwers and Anselmino, Abstr., 1904, i, 736).

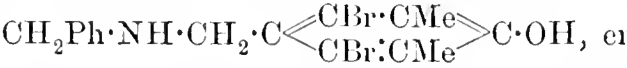
The *methylamine* derivative, $NMe(CH_2\cdot C_6Me_2Br_2\cdot OMe)_2$, of 3 : 6-dibromo-4-methoxy-ψ-cumyl bromide (Auwers and Reichel, Abstr., 1904, i, 997) melts at 149° and remains unchanged when boiled with dilute sodium hydroxide, glacial acetic acid, or acetic anhydride. The *diamylamine* derivative, $N(C_5H_{11})_2\cdot CH_2\cdot C_6Me_2Br_2\cdot OMe$, melts at 158° and resembles the methylamine derivative in its stability.

The diamylamine derivative, $N(C_5H_{11})_2\cdot CH_2\cdot C_6Me_2Br_2\cdot OAc$, formed from dibromo-*p*-acetoxy-ψ-cumyl bromide, separates from methyl alcohol in small, white crystals, melts at 45—46°, remains unchanged when boiled with glacial acetic acid or acetic anhydride, and is only slightly hydrolysed by boiling aqueous sodium hydroxide.

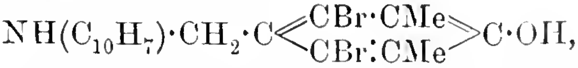
The *quaternary bromide*, $OMe\cdot C_6Me_2Br_2\cdot CH_2\cdot C_5NH_5Br$, formed from pyridine and dibromo-4-methoxy-ψ-cumyl bromide, crystallises from benzene, melts at 218—219°, and is decomposed into its components when boiled with glacial acetic acid or acetic anhydride.

With the exception of the piperidine and diamylamine derivatives of 3-bromo-4-hydroxy-ψ-cumyl bromide, and the diethylamine, diamylamine, methylaniline, and piperidine derivatives of 3 : 6-dibromo-4-hydroxy-ψ-cumyl bromide, the bases described in this paper remain unchanged when heated on the water-bath. G. Y.

Condensation Products of Organic Bases with ψ-Phenols of the Mesitol Series. Karl Auwers and A. Schrenk (*Annalen*, 1906, **344**, 227—255. Compare preceding abstracts).—The *ammonia* derivative, $N(CH_2\cdot C_6Me_2Br_2\cdot OH)_3$, formed by the action of ammonia on dibromo-*p*-hydroxymesityl bromide (Auwers and Allendorff, Abstr., 1899, i, 32), is obtained as a white, amorphous mass, which melts and decomposes at 250°, and is decomposed by boiling 10 per cent. aqueous sodium hydroxide, with formation of ammonia and tetrabromodihydroxytetramethyldiphenylmethane, melting at 232°, but yields only traces of ammonia when boiled with glacial acetic acid; the *triacetate*, $N(CH_2\cdot C_6Me_2Br_2\cdot OAc)_3$, formed by boiling the base with acetic anhydride, crystallises in small, colourless prisms and melts at 223—224°. The *methylamine* derivative, $NMe(CH_2\cdot C_6Me_2Br_2\cdot OH)_2$, melts at 154° and is partially decomposed by boiling dilute sodium hydroxide, with formation of the diphenylmethane derivative, which is formed together with the *acetate*,  $\mathrm{OAc\cdot CH_2\cdot C}\Big<\begin{matrix}\mathrm{CBr\cdot CMe}\\ \mathrm{CBr{:}CMe}\end{matrix}\Big>\mathrm{C\cdot OH}$, melting at 165—167°, when the base is treated with glacial acetic acid at the laboratory temperature; the action (1) of boiling glacial acetic acid on the base leads to the formation of the diacetate of dibromo-*p*-hydroxymesityl alcohol, together with a small quantity of the diphenylmethane derivative; (2) of boiling acetic anhydride to the formation of the diacetate and a small amount of a *product* which is insoluble in aqueous alkali hydroxides, contains nitrogen, and is probably the acetyl derivative of the base. When boiled with acetic anhydride, the hydrobromide of the methylamine base yields dibromo-*p*-acetoxymesityl bromide melting at 150—151°. Dibromo-*p*-hydroxymesityl ethyl ether, melting at 145—147°, is formed when the methylamine base is boiled with alcohol.

The *ethylamine* derivative, $NEt(CH_2\cdot C_6Me_2Br_2\cdot OH)_2$, crystallises in small, white needles, melts at 152°, yields ethylamine and the diphenylmethane derivative when heated on the water-bath, is converted completely into the diphenylmethane derivative by dilute aqueous sodium hydroxide at the laboratory temperature in twenty-four hours, and when treated with glacial acetic acid and acetic anhydride yields the same derivatives as does the methylamine derivative. The *benzylamine* derivative,  $\mathrm{CH_2Ph\cdot NH\cdot CH_2\cdot C}\Big<\begin{matrix}\mathrm{CBr\cdot CMe}\\ \mathrm{CBr{:}CMe}\end{matrix}\Big>\mathrm{C\cdot OH}$, crystallises in glistening prisms, melts at 127°, remains almost unchanged when heated on the water-bath, is partially decomposed by boiling aqueous sodium hydroxide with formation of benzylamine and the diphenylmethane derivative, and yields benzylamine and a mixture of products when boiled with glacial acetic acid; the *diacetyl* derivative, $CH_2Ph\cdot NAc\cdot CH_2\cdot C_6Me_2Br\cdot OAc$, formed by boiling the base with acetic anhydride, crystallises in needles and melts at 117—118°.

The *β-naphthylamine* derivative,



$$\mathrm{NH(C_{10}H_7)\cdot CH_2\cdot C}\Big<\begin{matrix}\mathrm{CBr\cdot CMe}\\ \mathrm{CBr{:}CMe}\end{matrix}\Big>\mathrm{C\cdot OH},$$

crystallises in delicate leaflets, melts at 233°, and remains unchanged when heated on the water-bath or boiled with aqueous sodium hydroxide or alcohol ; the *acetyl* derivative,

$$N(C_{10}H_7)Ac\cdot CH_2\cdot C_6Me_2Br_2\cdot OH,$$

formed by boiling the base with glacial acetic acid, crystallises in small, glistening prisms and melts at 207—208°, and the *diacetyl* derivative, $C_{23}H_{21}O_3NBr_2$, formed by boiling the base with acetic anhydride, crystallises in light yellow needles and melts at 182—184°. The *diethylamine* derivative, $NEt_2\cdot CH_2\cdot C_6Me_2Br_2\cdot OH$, crystallises in nodular aggregates of white needles, melts at 115—116°, and decomposes slowly at the laboratory temperature, quickly when heated on the water-bath ; it is completely decomposed by boiling aqueous sodium hydroxide, or, with formation of the diphenylmethane derivative and the mono- and di-acetates of dibromo-*p*-hydroxymesityl alcohol, when boiled with acetic acid ; the diacetate is formed by boiling the base with acetic anhydride. When boiled with alcohol, the diethylamine base yields dibromo-*p*-hydroxymesityl ethyl ether.

The *diamylamine* derivative, $N(C_5H_{11})_2\cdot CH_2<\begin{matrix}CBr\cdot CMe\\ CBr{:}CMe\end{matrix}>C\cdot OH$, crystallises in stellate aggregates of slender prisms, melts at 94°, and decomposes with formation of the diphenylmethane derivative when heated on the water-bath, or when recrystallised from hot solvents, or when boiled with dilute sodium hydroxide. The base yields the diphenylmethane derivative when treated with cold glacial acetic acid, or dibromo-*p*-acetoxymesityl acetate when boiled with the acid ; the action of boiling acetic anhydride on the base leads to the formation of the diacetates of dibromo-*p*-hydroxymesityl alcohol and the diphenylmethane derivative, melting at 159—160° and 244° respectively.

The methylaniline derivative, $NMePh\cdot CH_2\cdot C_6Me_2Br_2\cdot OH$, melts at 103—104°, decomposes with formation of methylaniline when heated on the water-bath, is decomposed only partially, forming the diphenylmethane derivative, when boiled with dilute sodium hydroxide, and yields the mono- and di-acetates of dibromo-*p*-hydroxymesityl alcohol when boiled with glacial acetic acid or acetic anhydride.

The piperidine derivative, $OH\cdot C_6Me_2Br_2\cdot CH_2\cdot C_5NH_{10}$, decomposes gradually, forming the diphenylmethane derivative when heated on the water-bath or when boiled with dilute sodium hydroxide, and yields the diacetate of dibromo-*p*-hydroxymesityl alcohol when boiled with glacial acetic acid or acetic anhydride.

The quaternary *bromide*, $OH\cdot C_6Me_2Br_2\cdot CH_2\cdot C_5NH_5Br$, melts at 260°, and when digested with cold dilute sodium hydroxide or carbonate yields the yellow substance, $C_9H_8OBr_2,C_5NH_5,H_2O$, melting at 242—245° (Auwers and Avery, Abstr., 1896, i, 150). When boiled with dilute sodium hydroxide, the quaternary bromide forms pyridine and the diphenylmethane derivative ; when boiled with glacial acetic acid or acetic anhydride, it yields the diacetate of dibromo-*p*-hydroxymesityl alcohol and dibromo-*p*-acetoxymesityl bromide.

The quaternary *bromide*, $OH\cdot C_6Me_2Br_2\cdot CH_2\cdot C_9NH_7Br$, melts at 266—267°, yields quinoline and the diphenylmethane when treated with cold dilute sodium hydroxide, and when boiled with glacial acetic acid yields the diphenylmethane derivative and dibromo-*p*-acetoxymesityl acetate, or, with acetic anhydride, the same diacetate together with dibromo-*p*-acetoxymesityl bromide.

The aniline derivative, $OH\cdot C_6Me_2Br_2\cdot CH_2\cdot NHPh$, yields traces of aniline when boiled with glacial acetic acid or dilute sodium hydroxide, and gradually decomposes when heated on the water-bath. The *acetyl* derivative, $OH\cdot C_6Me_2Br_2\cdot CH_2\cdot NPhAc$, melts at 238°; the *diacetyl* derivative, $OAc\cdot C_6Me_2Br_2\cdot CH_2\cdot NPhAc$, melts at 168—169·5°.

The *methylamine* derivative from dibromo-4-acetoxymesityl bromide, $NMe(CH_2\cdot C_6Me_2Br_2\cdot OAc)_2$, crystallises in small, white plates, melts at 218°, and remains unchanged when boiled with glacial acetic acid or acetic anhydride, or when heated on the water-bath. The *diamylamine* derivative, $OAc\cdot C_6Me_2Br_2\cdot CH_2\cdot N(C_5H_{11})_2$, crystallises in large, stout, colourless prisms, melts at 63°, and does not decompose when boiled with glacial acetic acid or acetic anhydride, or when heated on the water-bath. The *diethylamine* derivative, $OAc\cdot C_6Me_2Br_2\cdot CH_2\cdot NEt_2$, crystallises in glistening, stout rhombohedra, melts at 94°, and remains unchanged when boiled with glacial acetic acid or acetic anhydride.

*Dibromo-*p*-methoxymesityl bromide,*  $OMe\cdot C{<}\begin{smallmatrix}CMe\cdot CBr\\ CMe{:}CBr\end{smallmatrix}{>}C\cdot CH_2Br$, is prepared by the action of hydrogen bromide in glacial acetic acid solution on dibromo-*p*-methoxymesityl methyl ether, which is formed when dibromo-*p*-hydroxymesityl alcohol is boiled with methyl iodide and sodium in methyl-alcoholic solution. It crystallises in long, thin needles and melts at 143°. The *methylamine* derivative, $NMe(CH_2\cdot C_6Me_2Br_2\cdot OMe)_2$, which crystallises in small, white plates and melts at 180°, and the *diamylamine* derivative,

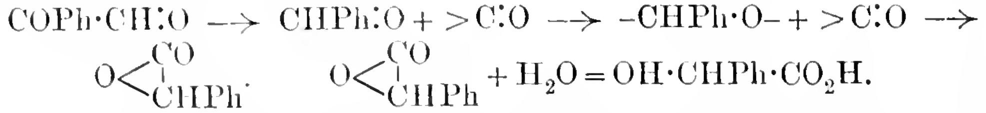
$$N(C_5H_{11})_2\cdot CH_2\cdot C_6Me_2Br_2\cdot OMe,$$

which crystallises in glistening, colourless prisms and melts at 164°, remain unchanged when boiled with glacial acetic acid or acetic anhydride, or when heated on the water-bath. The *pyridine* derivative, $OMe\cdot C_6Me_2Br_2\cdot CH_2\cdot C_5NH_5Br$, melts at 226° and decomposes into its components when boiled with glacial acetic acid.

4 : 6-*Dibromo-2-hydroxymesitylpiperidine*, $C_{14}H_{19}ONBr_2$, formed from piperidine and dibromo-2-hydroxymesityl bromide, crystallises in glistening, rhombic plates, melts at 91—92°, and when boiled with acetic anhydride yields dibromo-2-acetoxymesityl acetate melting at 98—99°.

With the exception of the ethyl-, benzyl-, diethyl-, and diamylamine, piperidine, and aniline derivatives of dibromo-*p*-hydroxymesityl bromide, the condensation products described above remain unchanged when heated on the water-bath. G. Y.

Behaviour of Benzoylcarbinol towards Alkalis and Oxidising Agents. Wm. Lloyd Evans (*Amer. Chem. J.*, 1906, 35, 115—144).—It has been shown by Nef (Abstr., 1905, i, 7) that copper acetate and sulphate are reduced by benzoylcarbinol in aqueous solution at the ordinary temperature to cuprous oxide and metallic copper respectively. The benzoylcarbinol is oxidised in these reactions to benzoylformaldehyde, which, when treated with aqueous sodium hydroxide or when heated with aqueous copper acetate or sulphate, is converted into *r*-mandelic acid. Nef concluded that the formation of *r*-mandelic acid from benzoylformaldehyde is due to a benzilic acid rearrangement, the benzoylformaldehyde being first dissociated into benzaldehyde and carbon monoxide in accordance with the following scheme:



$$\mathrm{COPh{\cdot}CH{:}O \longrightarrow CHPh{:}O + {>}C{:}O \longrightarrow -CHPh{\cdot}O- + {>}C{:}O \longrightarrow O{<}\begin{matrix}CO\\ |\\ CHPh\end{matrix} \qquad O{<}\begin{matrix}CO\\ |\\ CHPh\end{matrix} + H_2O = OH{\cdot}CHPh{\cdot}CO_2H.}$$

A study has been made of the behaviour of benzoylcarbinol and benzoylformaldehyde towards oxidising agents under various conditions. For details of the experiments, the original must be consulted. It has been found that benzoylformaldehyde is converted quantitatively into *r*-mandelic acid by soluble alkali hydroxides at the ordinary temperature and by aqueous copper acetate at 70—100°. The following facts support Nef's assumption that, in the formation of *r*-mandelic acid, the benzoylformaldehyde first undergoes dissociation into benzaldehyde and carbon monoxide. When benzoylformaldehyde is treated with freshly precipitated mercuric or silver oxide, it yields benzoic acid and carbon dioxide only; experiments with mandelic and benzoylformic acids have shown that this oxidation cannot involve the intermediate formation of these acids. With cupric oxide and alkali hydroxide, or with potassium ferricyanide and potassium hydroxide, the aldehyde is completely converted into *r*-mandelic acid. When the aldehyde is treated with cold aqueous potassium permanganate, benzoic acid is the sole product, but in presence of alkali hydroxide, benzoylformic, benzoic, and carbonic acids are produced, the benzoylformic acid being due to the oxidation of *r*-mandelic acid formed as an intermediate product. It is shown that these results can only be interpreted in accordance with the scheme suggested by Nef.

When benzoylcarbinol is heated at about 600°, it undergoes decomposition with evolution of gas and formation of benzene and benzaldehyde, whence it is concluded that the compound is dissociated by heat into benzaldehyde and formaldehyde.

If bromoacetophenone is treated with copper sulphate and sodium hydroxide at the ordinary temperature, it is converted into mandelic acid, whilst at 100°, benzoic, mandelic, and benzoylformic [phenylglyoxylic] acids are produced.

By the oxidation of acetophenone with potassium ferricyanide and potassium hydroxide, phenylglyoxylic and benzoic acids are formed, but no trace of mandelic acid is produced; it is evident, therefore, that this reaction does not proceed in a manner analogous to the oxidation of benzoylcarbinol and bromoacetophenone.

When benzoylcarbinol is treated with alkali hydroxide, alcoholic potassium hydroxide, or sodium ethoxide, a dark yellow, non-volatile, resinous product is formed, together with a small quantity of benzoic acid and traces of *trans*-tribenzoyl*cyclo*trimethylene.

Paal and Schulze (Abstr., 1903, i, 707) have assigned the formula $\mathrm{OH{\cdot}CPh{:}CBr{\cdot}CH{:}CPh{\cdot}OH}$ to their α- and β-bromodiphenacyls. A number of objections are raised to the validity of this formula, and evidence is adduced in favour of the formulæ $\mathrm{Ph{\cdot}CO{\cdot}CH_2{\cdot}\underset{\substack{|\\ BrCH}}{CO}{\cdot}Ph}$ and $\mathrm{Ph{\cdot}CO{\cdot}CH_2{\cdot}\underset{\substack{|\\ HCBr}}{CO}{\cdot}Ph}$, the former representing the α-compound or *cis*-α-

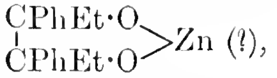
phenacyloxy-ω-bromostyrene, and the latter the β-compound or the *trans*-modification.

When α- and β-bromodiphenacyls are treated with a solution of fused sodium acetate in acetic acid at 100°, 66—68 per cent. of the theoretical quantity of benzoylcarbinyl acetate is produced. The α- and β-acetoxydiphenacyls on similar treatment also give a large yield of benzoylcarbinyl acetate. When α- and β-dibromophenacyl are reduced with zinc dust and alcohol, the chief product of the reaction is a non-volatile *oil*, probably α-phenacyloxystyrene, $CH_2{:}CPh\cdot O\cdot CH_2Bz$, small quantities of diphenacyl and acetophenone being also formed.

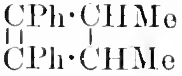
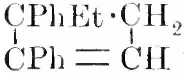
If α- or β-bromophenacyl is heated in a sealed tube for six hours at 100° with a solution of potassium formate in methyl alcohol, β-*hydroxydiphenacyl* is obtained, which crystallises from hot benzene in microscopic needles, melts at 175—178°, and when heated with fused sodium acetate and glacial acetic acid yields benzoylcarbinyl acetate together with a non-volatile tarry product.

The existence of Paal and Schulze's δ-iodophenacyl (Abstr., 1903, i, 709) is regarded as very doubtful, and it is suggested that it consists merely of the β-isomeride. E. G.

The Pinacone from Phenyl Ethyl Ketone. HEDWIG STERN (*Monatsh.*, 1905, **26**, 1559—1567. Compare Barry, this Journal, 1874, 74).—When reduced with sodium and aqueous sodium carbonate, phenyl ethyl ketone yields a mixture of phenylethylcarbinol and the unchanged ketone, boiling at 110—180° under 26 mm. pressure, and the *pinacone*, $OH\cdot CPhEt\cdot CPhEt\cdot OH$, boiling at 210° under the same pressure. The pinacone, which is obtained in a yield of 8 per cent. of the theoretical, crystallises in glistening, white plates, melts at 132°, is readily soluble in alcohol, ether, acetone, toluene, or carbon disulphide, but is insoluble in water, and remains unchanged when heated with 20 per cent. sulphuric acid on the water-bath or at 120°, or when boiled with acetic anhydride and sodium acetate. When oxidised with chromic acid in glacial acetic acid solution, it yields phenyl ethyl ketone boiling at 211°. In toluene solution, the pinacone interacts with zinc ethyl, with development of heat and formation of a *substance*,

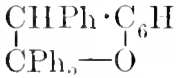


$$\begin{array}{l}\text{CPhEt}\cdot\text{O}\\ |\\ \text{CPhEt}\cdot\text{O}\end{array}\!\!>\text{Zn (?)},$$

which is decomposed by water, forming zinc hydroxide and regenerating the pinacone. When boiled with acetyl chloride, the pinacone yields (*a*) a small quantity of an oil, which boils at 211°, and is probably a mixture of phenyl ethyl ketone and phenylethylcarbinol, and (*b*) an unsaturated *hydrocarbon*,  $\begin{array}{ll}\text{CPh}\cdot & \text{CHMe}\\ \| & |\\ \text{CPh}\cdot & \text{CHMe}\end{array}$ or  $\begin{array}{ll}\text{CPhEt}\cdot & \text{CH}_2\\ | & |\\ \text{CPh} = & \text{CH}\end{array}$, which crystallises in white leaflets resembling mica, melts at 99°, and boils at 158° under 8 mm. pressure. It forms a *dibromide*, $C_{18}H_{18}Br_2$, which is obtained in yellow crystals, decomposes at 90°, and is soluble in carbon disulphide. G. Y.

Constitution of α- and β-Benzopinacolins. FRIEDRICH WERTHEIMER (*Monatsh.*, 1905, **26**, 1533—1544. Compare Thörner and Zincke, Abstr., 1878, 222, 425, 874; Lieben, Abstr., 1905, i, 167).—The benzopinacolins are obtained in similar yields by Thörner and Zincke's (*loc. cit.*) and Paal's (Abstr., 1884, 1167) methods of preparation. Of the product obtained by Paal's method, 20—25 per cent. consists of the α-isomeride. Tables are given showing the melting points of mixtures containing varying amounts of the α- and β-isomerides; that containing 27 per cent. of α-benzopinacolin melts at about 158·6°.

The α- and β-benzopinacolins do not form oximes, remain unchanged when heated with water at 190—200°, and, contrary to Delacre's statement (*Beilstein*, III, 264), do not interact with zinc ethyl at 130—140°. They are not oxidised by potassium permanganate in sulphuric acid solution on the water-bath, and are not reduced by aluminium amalgam and boiling alcohol.

β-Benzopinacolin remains unaltered when treated with zinc dust in glacial acetic solution, whilst the same treatment converts α-benzopinacolin into the mixture of the two isomerides melting at 159°. They do not form acetyl derivatives when heated with acetic anhydride and sodium acetate at 137°. When boiled with alcoholic potassium hydroxide in a reflux apparatus, α-benzopinacolin remains unchanged, whilst the β-isomeride yields triphenylmethane and benzoic acid. γ-Benzopinacolin must be an oxide, but not the αβ-oxide, and may have the structure  $\begin{array}{l}CHPh\cdot C_6H_4 \\ | \qquad\quad | \\ CPh_2—O\end{array}$; the ease with which α-benzopinacolin is converted into its β-isomeride, and the fact that both yield the same tetranitro-derivative (Biltz, Abstr., 1897, i, 523), show that they must be similarly constituted. G. Y.

Cholesterol. III. Otto Diels and Emil Abderhalden (*Ber.*, 1906, 39, 884—890. Compare Abstr., 1904, i, 880; Windaus and Stein, *ibid.*, 1010).—The authors have studied the question as to the position of the alcohol group in the cholesterol molecule relatively to the double linking. By the action of hydroxylamine on cholestenone, there was formed, in addition to the normal oxime, a second substance, which was probably a compound formed by the addition of hydroxylamine to cholestenone, the addition taking place at the double linking; this behaviour appears to indicate that cholestenone is an αβ-unsaturated ketone, a view which the authors adduce with reserve.

When cholesterol is reduced by sodium and boiling amyl alcohol, the reduction takes place at the double linking, and the saturated alcohol, α-cholestanol, $C_{27}H_{48}O$, is formed according to the equation $C_{27}H_{46}O + H_2 = C_{27}H_{48}O$. Cholestenone, when similarly reduced, forms the isomeric β-cholestanol. Those results accord with the supposition that cholesterol and cholestenone are αβ-unsaturated compounds. α-*Cholestanol* is entirely different from Bondzyński and Humnicki's coprosterol. It begins to soften at 117—118° and melts completely at 126—127°; when quickly heated, softening also begins at 118°, but the melting is complete at 124—125°. α-Cholestanol separates from ethyl alcohol, acetone, or ethyl acetate in prisms or plates. A saturated solution in acetic anhydride gives an indigo-blue coloration with concentrated sulphuric acid. Its *benzoyl* derivative softens at 126° and melts at 128—129°. When oxidised in glacial acetic acid solution by chromic acid, α-cholestanol forms *α-cholestanone*, $C_{27}H_{46}O$, which crystallises in prisms, softens at about 116°, and melts at 118—119°.

β-Cholestanol, $C_{27}H_{48}O$, formed by the reduction of cholestenone by boiling amyl alcohol and sodium, softens at about 140° and melts at 142—143°. When oxidised in glacial acetic acid solution by chromic acid, it forms *β-cholestanone*, $C_{27}H_{46}O$, which melts at 128—129°.

A. McK.

Isomorphous Substitution of the Elements Fluorine, Chlorine, Bromine, and Iodine in Organic Molecules. F. M. Jaeger (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, **8**, 613—623).—Methyl *p*-iodobenzoate crystallises in colourless needles melting at 114° and isomorphous with the analogous bromine compound. Crystallographical and physical facts are adduced to prove that the three halogenated esters of *p*-benzoic acid are dimorphous. E. F. A.

Methyl Amino-*p*-dimethylaminobenzoate. Frédéric Reverdin and Ernest Delétra (*Ber.*, 1906, **39**, 971—974).—The nitration of methyl *p*-dimethylaminobenzoate with nitric acid of sp. gr. 1·34 readily yields a *mononitro*-derivative, which melts at 71·5° and is reduced by tin and hydrochloric acid to the *amino*-compound, the *hydrochloride* of which forms white leaflets and melts at 228°. The *acetyl* compound, $C_{12}H_{16}O_3N_2$, melts at 232°. The *picrate* forms yellow crystals and explodes on heating. The base forms a condensation product with chlorodinitrobenzene which melts and decomposes at 253—254°. The base is readily diazotised and yields dyes of no practical interest.

Methyl hydroxy-p-*dimethylaminobenzoate*, $C_{10}H_{13}O_3N$, crystallises in long prisms and melts at 176·5°. The *barium* derivative forms glassy, red leaflets. C. S.

Sulphobenzoic Acids and their Nitro-derivatives obtained by the Action of Anhydrous Nitric Acid. Herman J. Taverne (*Rec. trav. chim.*, 1906, **25**, 50—74).—*o*-Sulphobenzoic acid crystallises with $3H_2O$ and melts at 70°; the anhydrous acid melts at 141° (compare Krannich, Abstr., 1901, i, 153).

5-*Nitro-2-sulphobenzoic acid* is prepared by dissolving *o*-sulphobenzoic acid in excess of anhydrous nitric acid, evaporating the excess of acid at a temperature not exceeding 50°, and exposing the residue under reduced pressure over sulphuric acid. The pure acid (hydrated) regenerated from the recrystallised *potassium* salt melts at 105°, is soluble in water and alcohol, slightly so in ether, and insoluble in benzene; the anhydrous acid is very hygroscopic and melts at 153°. The constitution of the acid was determined by its conversion into 2-chloro-5-nitrobenzoic acid by the action of phosphorus pentachloride, preliminary trials with sulphobenzoic and nitrosulphobenzoic acids having shown that this reagent could safely be used for this purpose.

m-Sulphobenzoic acid was prepared by hydrolysing ethyl *m*-sulphaminobenzoate with sulphuric acid or by sulphonating benzoic acid (compare Gattermann, Abstr., 1891, 1226). It forms efflorescent crystals with $2H_2O$, melts at 98°, and on exposure in a vacuous desiccator slowly becomes anhydrous and then melts at 141°. When nitrated by the method already described, it yields 2-*nitro-3-sulpho-*

benzoic acid, which may be identical with that prepared by Limpricht and Uslar (*Annalen*, 1858, **106**, 27). It crystallises with H_2O, melts at 96°, becomes anhydrous when dried in a vacuous desiccator over sulphuric acid, and then melts at 159·5°. The constitution of the acid was determined by its conversion into 2 : 3-dichlorobenzoic acid (Seelig, Abstr., 1887, 362) by the action of phosphorus pentachloride.

p-*Sulphobenzoic acid* was prepared either from *p*-sulphaminobenzoic acid or by the oxidation of toluene-*p*-sulphonic acid. It forms efflorescent crystals with $3H_2O$, melts at 94°, slowly becomes anhydrous when exposed in a vacuous desiccator over sulphuric acid, and then melts at 259—260°. When nitrated with anhydrous nitric acid or with a mixture of nitric and sulphuric acids, it yields 3-*nitro*-4-*sulphobenzoic acid*, which crystallises with $2H_2O$ and melts at 125—126°; the anhydrous acid melts at 159° (compare Hart, Abstr., 1881, 1144). When treated with phosphorus pentachloride, this yields a mixture of 3-nitro-4-chlorobenzoic (m. p. 179°) and 3 : 4-dichlorobenzoic acids (m. p. 201°).

The analogies observed between the results of the nitration of the chlorobenzoic acids (Montagne, Abstr., 1900, i, 491) and the sulphobenzoic acids, and the changes in melting points of the members of the two series of acids resulting from the introduction of a nitro-group are discussed in the original. T. A. H.

Stereochemistry of the Cinnamic Acids. EMIL ERLENMEYER, jun. (*Ber.*, 1906, **39**, 788—791. Compare Erlenmeyer, Abstr., 1883, 196; 1891, 1482; 1896, i, 302).—*r*-α-Bromo-β-phenyl-β-lactic acid is resolved into its active components by means of cinchonine, the salt of the *d*-acid crystallising out first, or by means of strychnine; the d-*acid* melts at 118° and has $[\alpha]_D$ +22·6°.

r-α-Chloro-β-phenyl-β-lactic acid and *r*-dibromohydrocinnamic acid are resolved by means of strychnine. *d*-α-*Chloro*-β-*phenyl*-β-*lactic acid* melts at 116° and has $[\alpha]_D$ +26·11°. *l*-Dibromohydrocinnamic acid has $[\alpha]_D$ −68·3°, and when boiled with water yields *d*-α-bromo-β-phenyl-β-lactic acid.

r-α-Iodo-β-phenyl-β-lactic acid is resolved by means of cinchonine; the d *acid* melts at 122° and has $[\alpha]_D$ +17°.

Sodium *l*-oxyphenylacrylic acid, having $[\alpha]_D$ −157·89°, is obtained by the action of aqueous sodium hydroxide on *d*-α-chloro- and on *d*-α-iodo-β-phenyl-β-lactic acids, and when treated with hydrogen chloride yields *d*-β-chloro-β-phenyl-α-lactic acid, melting at 144° and having $[\alpha]_D$ −71·7°.

d-β-Phenyl-β-lactic acid, formed by reduction of *d*-α-bromo-β-phenyl-β-lactic acid, melts at 116° and has $[\alpha]_D$ +19°.

The oily by-product obtained in Erlenmeyer and Lipp's preparation of chlorophenyl-lactic acid (Abstr., 1883, 992), when resolved by means of strychnine, yields two chlorophenyl-lactic acids, having $[\alpha]_D$ −16·62° and 13·76° respectively. G. Y.

Cinnamylideneacetic Acid [Styrylacrylic Acid] and some of its Transformation Products. ARTHUR MICHAEL and WIGHTMAN W. GARNER (*Amer. Chem. J.*, 1906, **35**, 258—267).—An improved method is described for the preparation of αβ-dibromo-δ-phenylpentenoic acid. When this acid (1 mol.) is treated with alcoholic potassium hydroxide (2 mols.), a product is obtained consisting of at least two bromo-δ-phenylpentenoic acids, which do not appear to be stereoisomerides, as the melting point (67—75°) of the mixture remains unchanged after repeated fusion. When the mixture is converted into the ethyl ester and the latter is boiled with alcoholic potassium hydroxide, a propiolic derivative is not obtained, but styrylacrylic acid is produced. *Ethyl δ-phenyl-Δ^{β}-pentenoate* was obtained as an oil boiling at 178° under 25 mm. pressure, and was converted into the dibromo-derivative by the action of a solution of bromine in carbon disulphide. On treating this substance with alcoholic potassium hydroxide, an uncrystallisable product was obtained which was converted into the ethyl ester, which boiled at 178—184° under 8—11 mm. pressure, but suffered decomposition, and was therefore unsuitable for further experiments.

Fittig (Abstr., 1895, i, 204) has shown that when Δ^{β}-unsaturated acids which contain an alkyl or a benzyl group are boiled with alkali hydroxide, they are mainly converted into the Δ^{α}-isomerides, but that the latter are partly changed into β-hydroxy-acids, which undergo partial conversion into the original Δ^{β}-acids. If, however, the alkyl or benzyl group is replaced by phenyl, only traces of the acid undergo such a rearrangement. If this intramolecular rearrangement in bromo-δ-phenyl-Δ^{β}-pentenoic acid precedes the elimination of hydrogen bromide, the following change would occur:

$$CH_2Ph\cdot CH{:}CH\cdot CHBr\cdot CO_2H \longrightarrow CH_2Ph\cdot CH_2\cdot CH{:}CBr\cdot CO_2H.$$

In order to obtain evidence on this point, a number of aromatic acids were oxidised with potassium permanganate under different conditions. It was found that acids of the cinnamic acid type, such as cinnamic, α-bromocinnamic, α-ethylcinnamic, and α-butylcinnamic acids invariably yield benzaldehyde when oxidised in presence of dilute sodium carbonate or strong potassium hydroxide. Phenylacetic acid gives benzaldehyde when dissolved in dilute sodium carbonate, but does not yield the aldehyde in presence of strong potassium hydroxide. β-Phenylpropionic acid does not furnish benzaldehyde either in presence of sodium carbonate or alkali hydroxide. δ-Phenyl-Δ^{α}-pentenoic acid gives the aldehyde in presence of alkali hydroxide, but the aldehyde is not formed by the oxidation of the free acid. The difference in the behaviour of β-phenylpropionic acid and δ-phenyl-Δ^{α} pentenoic acid is probably due to the action of the alkali hydroxide on the latter, converting it partially into the Δ^{β}-acid, which yields benzaldehyde on oxidation. The mixture of bromo-acids produced by the action of alcoholic potassium hydroxide on αβ-dibromo-δ-phenylpentenoic acid yields benzaldehyde when oxidised in the free state, and also in presence of sodium carbonate or potassium hydroxide. It is suggested, therefore, that at least a part of the mixture of bromo-acids is converted into an acid in which the double linking is nearer to the phenyl than it is in a Δ^{α}-acid, and that the production of styrylacrylic acid takes place without the intermediate formation of a propiolic derivative.

β-Phenylpropaldehyde *semicarbazone* crystallises in colourless leaflets and melts at 125°. E. G.

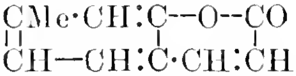
Condensation of Acetylenic Nitriles with Phenols. General Method of Synthesis of β-Substituted β-Phenoxyacrylonitriles. CHARLES MOUREU and I. LAZENNEC (*Compt. rend.*, 1906, **142**, 450—451. Compare this vol., i, 148; Moureu, Abstr., 1903, i, 698; 1904, i, 286; Moureu and Brachin, Abstr., 1904, i, 811; Ruhemann and Beddow, Trans., 1900, **77**, 984, 1119; Ruhemann and Stapleton, *ibid.*, 1179).—The β substituted β-phenoxyacrylonitriles are readily prepared by heating at 120—140° a mixture of the sodium derivative of the phenol and the acetylenic nitrile. *β-Phenoxy-β-amylacrylonitrile*, $C_5H_{11}\cdot C(OPh):CH\cdot CN$, boils at 175—178° under 15 mm. pressure; o-*tolyloxy-β-hexyl-β-acrylonitrile*, $C_6H_{13}\cdot C(O\cdot C_6H_4Me):CH\cdot CN$, boils at 195—196° under 15 mm. pressure; *β-phenoxy-β-phenylacrylonitrile*, $OPh\cdot CPh:CH\cdot CN$, melts at 85—86°; o-*tolyloxy-β-phenyl-β-acrylonitrile*, $C_6H_4Me\cdot O\cdot CPh:CH\cdot CN$, melts at 104—105°; *β-thymoxy-β-phenylacrylonitrile*, $C_6H_3MePr^{\beta}\cdot O\cdot CPh:CH\cdot CN$, boils at 226—229° under 11 mm. pressure, and *β-guaiacoxy-β-phenylacrylonitrile*,

$$OMe\cdot C_6H_4\cdot O\cdot CPh:CH\cdot CN,$$

melts at 90—91°. These compounds are hydrolysed by alcoholic potassium hydroxide to form the corresponding ketone and phenol, thus β-phenoxy-β-phenylacrylonitrile yields acetophenone and phenol.

M. A. W.

Coumarins from *m*-Cresol. K. FRIES and W. KLOSTERMANN (*Ber.*, 1906, **39**, 871—875).—Whilst the formation of coumarins from phenol, *o*-cresol, or *p*-cresol and malic acid or ethyl acetoacetate respectively proceeds with difficulty according to Pechmann's method, it takes place readily with *m*-cresol.

7-Methylcoumarin, 

$$\begin{array}{l}\mathrm{CMe\cdot CH:C{-}{-}O{-}{-}CO}\\ \|\qquad\qquad\quad |\qquad\quad\ \ |\\ \mathrm{CH{-}CH:C\cdot CH:CH}\end{array}$$

prepared by the addition of sulphuric acid to a mixture of *m*-cresol and malic acid, separates from dilute alcohol in needles and melts at 128°. The authors' observations with this substance are at variance with those of Schmidt (*Inaug. Diss.*, Rostock, 1897), who prepared it by the Perkin synthesis from sodium acetate and *m*-homosalicylaldehyde. Chuit and Bolsing (this vol., i, 185) give 126° as the melting point. When fused with sodium hydroxide, 7-methylcoumarin forms 4-methylsalicylic acid, melting at 177°. When boiled for several hours with sodium ethoxide, 7-methylcoumarin forms ethyl 4-methylcoumarate, melting at 105°, from which 4-methylcoumaric acid is formed on saponification; the latter separates from alcohol in needles and decomposes at 195°.

4 : 7 *Dimethylcoumarin*, $C_9H_4O_2Me_2$, prepared by the action of sulphuric acid on a mixture of *m*-cresol and ethyl acetoacetate, separates from alcohol in needles and melts at 132°. When fused with sodium hydroxide, it forms 4-methylsalicylic acid. When boiled for five hours with 33 per cent. aqueous potassium hydroxide, it is converted into β-4-dimethylcoumaric acid, which separates from water in needles and melts and decomposes at 142°. When boiled with sodium ethoxide, it does not form coumaric acid, but is converted into the *compound*, $C_{21}H_{22}O_3$, which contains a phenolic group and is presumably bisdimethylhydrocoumarone ketone.

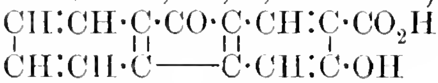
3 : 4 : 7-*Trimethylcoumarin*, prepared by the action of sulphuric acid

on a mixture of *m*-cresol and methyl ethylacetoacetate, separates from alcohol in glistening needles and melts at 114°. It is not decomposed when boiled with aqueous potassium hydroxide or with sodium ethoxide.
A. McK.

Chlorination of Indigotin. Badische Anilin- & Soda-Fabrik (D.R.-P. 163280).—It is not possible to chlorinate indigotin by the methods employed for bromination, as decomposition then occurs. Indigo-white and its homologues may be chlorinated in strong hydrochloric acid solution, the temperature not being allowed to rise above 20°. To prepare a monochloro-derivative, 2 mols. of chlorine are required, 1 mol. being necessary to oxidise the indigo-white to indigotin. The intermediate formation of a chloroindigo-white may be recognised, but the isolation of this compound is not practicable.

Chloroindigotin forms a blue powder, dissolving more readily in organic solvents than indigotin. It sublimes and partially decomposes on heating, and is reduced by alkali hyposulphites. By the employment of larger quantities of chlorine, higher chlorinated products may be prepared.
C. H. D.

New Syntheses of Derivatives of Fluorene and of Diphenyl. Giorgio Errera and G. La Spada (*Gazzetta*, 1905, 35, ii, 539—553).—3-*Hydroxyfluorenone-2-carboxylic acid*,



$$\begin{array}{l}\mathrm{CH{:}CH{\cdot}C{\cdot}CO{\cdot}C{\cdot}CH{:}C{\cdot}CO_2H} \\ \mathrm{CH{:}CH{\cdot}C\text{——}C{\cdot}CH{:}C{\cdot}OH}\end{array},$$

prepared by the action of 25 per cent. potassium hydroxide solution on ethyl indandionemethenylacetoacetate, separates in yellow needles, melts and decomposes at 277—279°, and is soluble in acetic acid or xylene and, to a slight extent, in water, alcohol, or light petroleum. It acts as a dibasic acid. The *potassium*, *sodium* ($+2H_2O$), and *silver* salts were prepared. The *methyl* ester, $C_{15}H_{10}O_4$, crystallises from xylene in yellow needles melting at 250° and dissolves slightly in methyl or ethyl alcohol or light petroleum, and readily in dilute solutions of the alkali hydroxides.

Methyl 3-*methoxyfluorenone-2-carboxylate*, $OMe{\cdot}C_{13}H_6O{\cdot}CO_2Me$, prepared from the corresponding hydroxy-ester by the action of potassium hydroxide solution and methyl sulphate, crystallises from light petroleum in yellow needles melting at 169° and is slightly soluble in methyl alcohol. The corresponding *acid*, $C_{15}H_{10}O_4$, crystallises from acetic acid in minute, yellow needles melting and decomposing at 261° and dissolves sparingly in methyl or ethyl alcohol or light petroleum and, in larger amount, in solutions of the alkali hydroxides or carbonates, yielding orange-red liquids.

3-*Hydroxyfluorenone*, $C_{13}H_7O{\cdot}OH$, prepared by maintaining 3-hydroxyfluorenone-2-carboxylic acid for some time at its melting point, crystallises from xylene in minute, yellow needles melting at 228—229°, and dissolves sparingly in light petroleum and readily in alcohol; it is dissolved by concentrated sulphuric acid, giving a violet liquid, and by alkali hydroxide or carbonates, yielding orange-red solutions. Its *benzoyl* derivative, $C_{13}H_7O{\cdot}OBz$, crystallises from aqueous alcohol in shining, golden-yellow plates melting at 150°. The *acetyl* derivative, $C_{13}H_7O{\cdot}OAc$, crystallises from alcohol in yellow needles melting at

115°. The *oxime*, $C_{13}H_8O·NOH$, separates from light petroleum as a brown, crystalline powder melting and decomposing at 187—188°, and dissolves sparingly in water, readily in alcohol or acetic acid, and in solutions of bases giving intense orange colorations. The corresponding *methoxy*-compound, $C_{13}H_7O·OMe$, separates from light petroleum in yellow, crystalline incrustations melting at 96—97° and is readily soluble in alcohol.

3-*Hydroxydiphenyl-6-carboxylic acid*, $OH·C_{12}H_8·CO_2H$, prepared by the action of potassium hydroxide on the potassium derivative of 3-hydroxyfluorenone, crystallises from water in needles which contain H_2O and melt in their water of crystallisation at 123°; the anhydrous acid melts at 147°. It dissolves in alcohol or light petroleum. The acid dissolves in cold concentrated sulphuric acid, giving a colourless liquid which rapidly becomes violet and, on dilution with water, deposits 3-hydroxyfluorenone. The *sodium*, *potassium*, *silver*, and *calcium* ($+3H_2O$) salts are described.

3-*Hydroxydiphenyl*, $C_{12}H_9·OH$, prepared by the dry distillation of a mixture of calcium 3-hydroxydiphenyl-6-carboxylate and slaked lime, crystallises from light petroleum in shining, white needles melting at 75° and boils above 300°; it dissolves in cold alkali hydroxide solutions, in hot alkali carbonate solutions, in water sparingly, and in alcohol or light petroleum more readily. The *benzoyl* derivative, $C_{12}H_9·OBz$, crystallises from alcohol in silvery plates melting at 60—61°. T. H. P.

Butadiene Compounds. XV. Colour of Methoxy-derivatives of Mono-, Di-, and Tri-phenylfulgides. HANS STOBBE (*Ber.*, 1906, **39**, 761—769. Compare Abstr., 1904, i, 589, 672; this vol., i, 22, 91, 183).—The following table gives the colours of the fulgides and the wave-lengths of the spectrum; the first number denotes the beginning of the visible absorption, the following number the commencement of total absorption in $N/32$ solution in chloroform:

α-*p*-Methoxyphenyl-δδ-dimethylfulgide	Yellow	446	436
δ-Phenyl-α-*p*-methoxyphenylfulgide	Orange	494	479
δδ-Diphenyl-α-*p*-methoxyphenylfulgide	Orange-red	539	521
α-*o*-Methoxyphenyl-δδ-dimethylfulgide	Yellow	443	428
δδ-Diphenyl-α-*o*-methoxyphenylfulgide	Dark red	534	527
α-Phenyl-δδ-dimethylfulgide	White or light yellow	418	412
αδ-Diphenylfulgide	Citron-yellow	456	448
αδδ-Triphenylfulgide	Orange-red	537	513

The colour of the fulgides is not influenced by replacing the methoxy- by the ethoxy-group.

[With ALFRED LENZNER.]—α-p-*Methoxyphenyl-δδ-dimethylfulgenic acid*, $OMe·C_6H_4·CH:C(CO_2H)·C(CO_2H):CMe_2$, from anisaldehyde and ethyl dimethylitaconate, forms small, white crystals and melts, decomposes, and turns yellow at 226—227°. The *fulgide*, $C_{15}H_{14}O_4$, melts at 114·5°.

α-o-*Methoxyphenyl-δδ-dimethylfulgenic acid*, $C_{15}H_{16}O_5$, from *o*-methoxybenzaldehyde and ethyl dimethylitaconate, melts and decomposes at

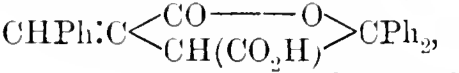
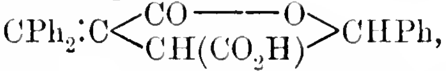
200°. The *fulgide*, $C_{15}H_{11}O_4$, melts at 97·5° and separates from carbon disulphide in glassy, yellow crystals which contain carbon disulphide and effloresce rapidly in the air.

[With Karl Kautzsch and Th. Badenhausen.]—δ-*Phenyl*-α-p-*methoxyphenylfulgenic acid* is obtained from anisaldehyde and diethylphenylitaconate and is white. The *fulgide*, $C_{19}H_{14}O_4$, melts at 144—147°.

[With Rudolf Nettel.]—δδ-*Diphenyl*-α-p-*methoxyphenylfulgenic acid*, $C_{25}H_{20}O_5$, from anisaldehyde and ethyl diphenylitaconate, separates from chloroform or benzene in white crystals containing 1 mol. of the solvent, the former compound melting and decomposing at 211°. The *sodium* and *barium* salts are described. The *fulgide*, $C_{25}H_{18}O_4$, melts at 194°.

α-o-*Ethoxytriphenylfulgenic acid*, $C_{26}H_{22}O_5$, from *o*-ethoxybenzaldehyde and ethyl diphenylitaconate, forms yellow crystals containing C_2H_6O. The *sodium* salt is described. The *fulgide*, $C_{26}H_{20}O_4$, melts at 181°, is stable towards water, and yields salts of the fulgenic acid by treatment with alkalis or piperidine.

[With Erich Benary.]—δδ-*Diphenyl*-α-o-*methoxyphenylfulgenic acid*, $C_{25}H_{20}O_5$, from *o*-methoxybenzaldehyde and ethyl diphenylitaconate, turns red at 205°, melts and decomposes at 229—231°, and separates from alcohol in yellow prisms which contain C_2H_6O and slowly effloresce in the air. The *sodium* salt is described. The *fulgide*, $C_{25}H_{18}O_4$, softens and melts at 200°. C. S.

Butadiene Derivatives. XVI. Anomalies in the Synthesis of Fulgenic Acids. Hans Stobbe and Th. Badenhausen (*Ber*., 1906, **39**, 769—772).—When benzaldehyde is condensed with ethyl γγ-diphenylitaconate in alcoholic solution containing sodium ethoxide, αδδ-triphenylfulgenic acid is obtained (Abstr., 1904, i, 672), but on attempting to prepare the latter acid by the interaction of benzophenone, ethyl phenylitaconate, and sodium ethoxide in ethereal solution, a lactonic acid, which is either γ-*diphenyl*-α-*benzylideneparaconic acid*,  $CHPh{:}C<\begin{matrix}CO\text{——}O\\CH(CO_2H)\end{matrix}>CPh_2$, or γ-*phenyl*-α-*diphenylmethyleneparaconic acid*,  $CPh_2{:}C<\begin{matrix}CO\text{——}O\\CH(CO_2H)\end{matrix}>CHPh$, is produced. It crystallises from chloroform or 60 per cent. acetic acid in white needles, melts at 203—205°, gives benzophenone on oxidation with potassium permanganate, and is converted into αδδ-triphenylfulgenic acid by boiling for two hours with alcoholic sodium hydroxide or ethoxide. αδδ-Triphenylfulgenic acid, however, cannot be converted into the lactonic acid by heating it with acetic anhydride containing a few drops of sulphuric acid.

The production of a lactonic acid under the conditions stated shows that the fulgenic acid syntheses probably take place through the intermediate formation of a derivative of paraconic acid as in the normal Fittig syntheses. In most cases, the paraconic acid is converted into the corresponding fulgenic acid by the action of the sodium ethoxide used in the syntheses. W. A. D.

Lichens and their Characteristic Constituents. X. OSWALD HESSE (*J. pr. Chem.*, 1906, [ii], 73, 113—176).—The author claims priority for the name chrysocetraric acid for the acid $C_{19}H_{16}O_6$ (Abstr., 1895, i, 299). Zopf's pinastric acid (Abstr., 1895, i, 297; 1905, i, 212) was not a pure substance.

The formula $C_{28}H_{22}O_7$, but not Zopf's formula ($C_{13}H_{10}O_3$), for rhizocarpic acid is in agreement with the conversion of the acid into nor-rhizocarpic acid (Abstr., 1899, i, 384), or, when heated with an excess of baryta in a sealed tube at 120°, into alcohol, carbon dioxide, and phenylacetic acid.

Usnea longissima, from Amani, in German East Africa, contains ramalic, *d*-usnic, and dirhizonic acids.

Dirhizonic acid, $C_{18}H_{16}O_5(OMe)_2$, crystallises in small, white needles, melts and decomposes at 189°, is readily soluble in ether, alcohol, acetone, or glacial acetic acid, and dissolves in dilute alkali hydroxides; the alcoholic solution is optically inactive and gives a blue coloration with ferric chloride, but not with bleaching powder. On prolonged boiling with aqueous baryta, the acid yields betorcinol methyl ether and carbon dioxide; the residue from the methoxyl determination contains betorcinol. The *potassium* ($2H_2O$), *sodium* ($2H_2O$), *barium* ($2H_2O$), *calcium* ($3H_2O$), and *copper* salts are described.

The substance observed previously in *Usnea barbata var. hirta*, and termed usnarin, is now found to be identical with atranorin. A specimen of this lichen from the island of St. Thomas, in the Gulf of Guinea, contained *d*-usnic and usnaric acids and *santhomic acid*, $C_{11}H_{14}O_4$, which crystallises in colourless, glistening prisms or delicate, white needles, melts and decomposes at 166°, is moderately soluble in water, and in alcoholic solution gives with ferric chloride a bluish-black, with bleaching-powder a bluish-violet, coloration.

A specimen of *Usnea barbata var. hirta*, from the east coast of Madras, contained *d*-usnic, usnaric, usnarinic, barbatic, and hirtaic acids.

Usnarinic acid, $C_9H_{10}O_4$, forms a colourless or slightly yellow, granular powder, assumes a brown colour at 200°, decomposes and chars at 240°, has a bitter after-taste, is readily soluble in hot alcohol or glacial acetic acid, and with ferric chloride gives a dark brownish-red coloration; on addition of a drop of moderately-concentrated potassium hydroxide, the acid becomes yellow, changes to red, dissolves in water, and on acidification yields a red, flocculent precipitate; with concentrated sulphuric acid, usnarinic acid gives a yellow coloration changing to red. The *ammonium*, *potassium*, and *sodium* salts are gelatinous.

Hirtaic acid, $C_{15}H_{21}O_5{\cdot}OMe$, crystallises in small, colourless, rhombic leaflets, sinters at 130°, melts at 136—137°, is readily soluble in ether, alcohol, acetone, glacial acetic acid, or concentrated aqueous potassium hydroxide, carbonate, or hydrogen carbonate, and gives a brownish-red coloration with ferric chloride. The *potassium*, *barium*, *calcium*, and *silver* salts are gelatinous. With concentrated sulphuric acid, hirtaic acid gives a yellow coloration, becoming red on warming; when heated with concentrated nitric acid, it forms a yellow nitro-derivative, and when boiled with hydriodic acid yields methyl iodide and *norhirtaic acid*.

Usnea barbata var. florida, from cinchona bark from the east coast of Madras, contains barbatic acid together with traces of usnaric and *d*-usnic acids.

Alectoria implexa, obtained from the Tarnovaner Wald, near Görz, contains atranorin and an *acid* which crystallises in small nodules, melts and decomposes at about 178°, and is not alectoric acid.

Contrary to Zopf's statement (Abstr., 1904, i, 1020), *Cornicularia aculeata* contains rangiformic acid.

Roccella phycopsis, from Paximadi Island (Crete), contains erythrin, oxyroccellic and oxalic acids, and *i*-erythritol.

Erythrin, the chromogen of *Roccella montagnei*, *R. fuciformis*, *R. peruensis*, and *R. physopsis*, is the ester of erythritol and lecanoric acid. Erythric acid, the chromogen of *Aspicilia calcarea farinosa*, is erythrolecanoric acid,

$$C_4H_6(OH)_3\cdot O\cdot C_6H_2Me(OH)\cdot CO\cdot O\cdot C_6H_2Me(OH)\cdot CO_2H.$$

Roccella peruensis (*R. fructectosa*; *R. cacticola*) has been re-examined and found to contain erythrin, erythritol, and oxalic acid.

Cetraria islandica, from the Cavalljoch in the Vorarlberg, contains proto-α-lichesteric acid. The same lichen from the Stubaital, in the Tyrol, contains protolichesteric and proto-α-lichesteric acids. When these acids are dissolved in dilute potassium hydroxide and a current of carbon dioxide passed through the solution, proto-α-lichesteric acid is precipitated first.

The comparison of triethylprotocetraric acid with cetraric acid has been repeated, and the identity of the two acids confirmed (see Abstr., 1905, i, 139). When heated with 97 per cent. alcohol containing a couple of drops of sulphuric acid in a sealed tube at 100°, cetraric acid yields carbon dioxide and triethylcetrol, which forms a blue solution in alcohol and separates as a greenish-blue, amorphous precipitate on dilution with water.

Parmelia tinctorum, from the Regenwald in Amani, German East Africa, contains atranorin and 2½ per cent. of lecanoric acid.

Contrary to Zopf's statement (Abstr., 1905, i, 790), conspersaic acid from *P. conspersa* is not identical with salazinic acid.

Ochrolechia pallescens (γ) *parella*, from Orcival, in Auvergne, contains parellic and ochrolechiasic acids in the proportion 1 : 7 or 8. Ochrolechiasic acid, $C_{22}H_{14}O_9$, melts at 282° and does not contain a methoxyl group; the *barium* and *calcium* salts crystallise in small needles; the *potassium* salt forms colourless needles. The acid is precipitated unchanged on acidification of its freshly-prepared solution in dilute potassium hydroxide, but after some minutes it is converted into *ochric acid*, which crystallises in concentric aggregates of stout prisms, melts and evolves carbon dioxide at 230°, and gives a violet coloration with ferric chloride or a yellow coloration with bleaching powder, and when warmed with concentrated sulphuric acid becomes yellow and finally dark brown.

Sterile *Pertusaria lactea*, from Orcival, in Auvergne, contains lecanoric acid, ochrolechiasic acid, which may be identical with Zopf's violaric acid (Abstr., 1905, i, 212), traces of parellic acid, paric acid, and an *acid* which melts at 286° and resembles ochrolechiasic acid.

Hämatomma coccineum var.?, from a wall near Wildbad, contains coccic acid, atranorin, zeorin melting at 236° (m. p. 247—252°; Zopf, Abstr., 1896, i, 104), and *hydrohämatommin*, $C_{10}H_{18}O$, which crystallises in delicate, white needles, melts at 101°, is tasteless, dissolves readily in alcohol, ether, chloroform, or glacial acetic acid, is neutral, gives with concentrated sulphuric acid a red coloration, becoming blackish-brown when warmed, and when shaken with chloroform and sulphuric acid colours the acid brown, the chloroform red.

Atranorin is a condensation product of betorcinol methyl ester with hämatommic acid, $CO_2Me \cdot C_8H_8O_2 \cdot CO \cdot C_8H_9O_3$. Contrary to the statement of Zopf (Abstr., 1905, i, 212), *Pulveraria chlorina* [*Lepraria* (*Lepra*) *chlorina*] contains small amounts of lepraric acid. It does not give a coloration with alcoholic potassium hydroxide. *L. xanthina*, a sterile, yellow lichen, obtained from Gampertonatal in the Vorarlberg, contains physcion and gives a red coloration with potassium hydroxide.

L. latebrarum, obtained from the porphyrite cliff behind the old castle in Baden-Baden, contains atranorin, an indifferent *substance* crystallising in needles, leprariaic and oxyroccellic acids, and *neobraric acid*, which melts at a few degrees higher than oxyroccellic acid.

The action of dilute potassium hydroxide on parellic acid,

$$CO_2Me \cdot C_{17}H_{11}O_3(CO_2H)_2,$$

leads to the formation of *paric acid*, $CO_2Me \cdot C_{13}H_{10}O_4 \cdot CO_2H$, which crystallises in stout, colourless prisms, melts and decomposes at about 230°, gives with ferric chloride an intense blue, with bleaching powder a yellow coloration, and when boiled with aqueous baryta yields carbon dioxide and *parinic acid*, $C_{13}H_{11}O_4 \cdot CO_2H$. This crystallises in delicate glistening needles containing H_2O, commences to become brown at 215°, decomposes at 225°, reddens litmus in alcoholic solution, and dissolves in concentrated sulphuric acid, forming a yellow solution which becomes deep yellow. The *ammonium* salt forms small needles; the *barium* salt, $(C_{14}H_{11}O_6)_2Ba,4H_2O$, crystallises in small, yellow needles.

G. Y.

Two Homosalicylaldehydes derived from *m*-Cresol. PH. CHUIT and FR. BOLSING (*Bull. Soc. chim.*, 1906, [iii], **35**, 129—143).—Tiemann and Schotten's supposed *m*-homosalicylaldehyde (Abstr., 1878, 875) has been found by the authors to consist of a mixture of two homosalicylaldehydes, which may be separated by recrystallisation of the mixed oximes from benzene or carbon disulphide, or by fractional distillation with steam from an aqueous solution of sodium carbonate, or by fractional crystallisation of the calcium or barium derivatives of the aldehydes from warm water.

a-m-*Homosalicylaldehyde* [Me : OH : COH = 1 : 3 : 4] crystallises in flattened, colourless needles from alcohol, has an odour recalling that of salicylaldehyde, melts at 59—59·8°, boils at 220·8° under 726 mm. pressure, and is slightly soluble in cold alcohol or warm water. It gives a violet coloration with ferric chloride and yellow with alkalis; the *sodium hydrogen sulphite* compound is crystalline and is decomposed by warm water. The *sodium*, *potassium*, *calcium*, and *barium* derivatives were prepared. The *oxime* crystallises from 50 per cent. alcohol in colourless spangles, melts at 108·5—109°, and is readily soluble in alcohol or benzene, and nearly insoluble in light petroleum.

The *phenylhydrazone* forms colourless, pearly spangles from alcohol and melts at 160—160·5°. The *semicarbazone* crystallises from alcohol, in which it is sparingly soluble, in colourless spangles, which assume a rose tint on exposure to light, melt at 254°, becoming solid and re-melting at 272°.

The *methyl ether* is best prepared by the action of methyl iodide (methylation is incomplete when methyl sulphate is used); it forms colourless needles, melts at 42—43°, boils at 263—264° under 720 mm. pressure, has a feeble odour in the cold, and gives no coloration with ferric chloride; its *oxime* melts at 122·8—123·5°. When fused with potassium hydroxide, the ether undergoes demethylation, yielding *a*-*m*-homosalicylic acid. When oxidised with potassium permanganate, it furnishes 3-methoxyterephthalic acid. The dimethyl ester of the latter melts at 71·5°, not 65°, as given by Baeyer and Tutein (Abstr., 1889, 1180).

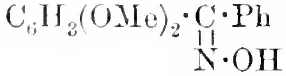
β-m-*Homosalicylaldehyde* [Me : OH : COH = 1 : 3 : 2] crystallises in long, colourless needles from water, melts at 31·4—31·9°, boils at 228·6° under 728 mm. pressure, and is readily soluble in benzene, slightly so in ether. It gives a violet coloration with ferric chloride, yellow with alkalis, and forms with sodium hydrogen sulphite a solid *additive product*, which is decomposed by hot water. The *sodium*, *potassium*, *calcium*, and *barium* derivatives are crystalline. The *oxime* melts at 111—112° and is readily soluble in alcohol; the *phenylhydrazone* forms bright yellow spangles and melts at 170·2° to 171·4°, and the *semicarbazone* colourless leaflets melting at 214° and re-melting at 244°.

The *methyl ether* crystallises from light petroleum in colourless leaflets, which become yellow on exposure to light, and melts at 41·5—42°. It gives no coloration with ferric chloride. The *oxime* separates from water in colourless needles and melts at 118·5—119·5°. On oxidation with permanganate, the methyl ether yields 3-*methoxy*-o-*toluic acid* [Me : CO_2H : OMe = 1 : 2 : 3]. This crystallises from water in colourless, flattened needles, melts at 139°, and gives no coloration with ferric chloride. The *methyl* ester is liquid. T. A. H.

cycloHexylacetone. Paul Freundler (*Compt. rend.*, 1906, **142**, 343—345. Compare Abstr., 1905, i, 890).—Magnesium hexahydrobenzyl iodide condenses with acetaldehyde to form *a*-*cyclo*hexyl-*β*-propyl alcohol, which, on oxidation, yields *cyclo*hexylacetone (Bouveault, Abstr., 1904, i, 61). *Hexahydrobenzyl iodide*, $C_6H_{11}·CH_2I$, prepared by the action of phosphorus tri-iodide or red phosphorus and iodine on the corresponding alcohol, boils at 97—99° under 18—19 mm. pressure. *a*-cyclo*Hexyl*iso*propyl alcohol*, $C_6H_{11}·CH_2·CHMe(OH)$, is a liquid with an agreeable odour, boiling at 201—202° under normal pressure and sparingly soluble in water. cyclo*Hexylacetone*, $C_6H_{11}·CH_2·COMe$, boils at 197° and has an odour similar to that of camphor; the *hydrogen sulphite* is sparingly soluble and the *semicarbazone* melts at 182·5°. M. A. W.

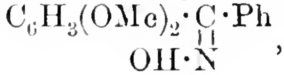
Fluorogen Groups. A Contributio to the Theory of Partial Valencies. Hugo Kauffmann (*Annalen*, 1906, **344**, 30—77. Compare Abstr., 1905, i, 280; Kauffmann and Beisswenger, *ibid.*).—Fluorescent substances contain two groups of different functions, one of which is the cause of fluorescence and has been termed the fluorogen; the name "luminophore" is now proposed for the other group, which is the source of luminescence. In aromatic compounds, the luminophore is the benzene ring, the activity of which varies with the nature and number of the substituting groups present, being greatest for *p*-diaminobenzene and dimethylaniline, and moderate for aniline and quinol and its ethers. Luminescence is produced by the action of radium rays or of Tesla rays (compare Kauffmann, Abstr., 1904, ii, 691). Tables are given of the comparative results obtained with derivatives of *p*-dimethoxybenzene, by determining the distance at which 5 mg. of radium bromide cause luminescence with and without the intervention of a sheet of zinc. Those derivatives of *p*-dimethoxybenzene which are fluorescent contain as substituting group the unsaturated carbonyl, carboxyl, or cyanogen group, or a group containing an ethylene linking. These fluorogens are also chromophores, but fluorescence is not caused always by the presence of a chromophoric group, probably because strong chromophores interfere, with the luminophoric activity of the benzene ring; thus, highly coloured derivatives of *p*-dimethoxybenzene are only slightly luminescent. The fluorescence of a substituted *p*-dimethoxybenzene containing the grouping $C_6H_3(OMe)_2\cdot C^{1^1}\cdot C^{1^2}$, is lessened or hindered by the introduction of a phenyl group in position 1^1, but is increased by a phenyl group in position 1^2. This is explained by means of Thiele's theory of partial valencies, and the conclusion drawn that a carbonyl group, or a group containing an ethylene linking, functions as a fluorogen the more strongly the more the partial valencies of the group are rendered inactive by the partial valency of the luminophore or benzene ring.

[With Adolf Grombach.]—2 : 5-*Dimethoxybenzophenone*, $C_{15}H_{14}O_3$, is formed together with a small quantity of 5-hydroxy-2-methoxybenzophenone by the action of benzoyl chloride on *p*-dimethoxybenzene in carbon disulphide solution in presence of aluminium chloride; it separates from methyl alcohol or light petroleum in yellow crystals, melts at 51°, boils at 225° under 30 mm. pressure, is readily soluble in most solvents, dissolves without decomposing in concentrated sulphuric acid, forming a brownish-red solution, and yields benzoic acid and *p*-dimethoxybenzene when fused with potassium hydroxide. The *phenylhydrazone*, $C_6H_3(OMe)_2\cdot CPh{:}N_2HPh$, formed by shaking the dimethyl ether with phenylhydrazine in glacial acetic acid solution, separates from alcohol in white crystals and melts at 126°. When boiled with hydroxylamine hydrochloride in alcoholic solution, the dimethyl ether yields two stereoisomeric *oximes*: the oxime



$$C_6H_3(OMe)_2\cdot\underset{\substack{\| \\ N\cdot OH}}{C}\cdot Ph$$

melts at 136° and is less soluble in aqueous sodium hydroxide than the more strongly acid stereoisomeride,



$$C_6H_3(OMe)_2\cdot\underset{\substack{\| \\ OH\cdot N}}{C}\cdot Ph$$

, which melts at 120°.

5-*Hydroxy-2-methoxybenzophenone*, $C_{14}H_{12}O_3$, formed by hydrolysis of the dimethyl ether with aluminum chloride at 70—80°, or with boiling concentrated hydriodic acid, separates from alcohol in large, stout, yellow crystals, melts at 78°, and when shaken with methyl sulphate and aqueous sodium hydroxide yields the dimethyl ether. The *phenylhydrazone*, $OH{\cdot}C_6H_3(OMe){\cdot}CPh{:}N_2HPh$, formed by the action of phenylhydrazine on the monomethyl ether in glacial acetic acid solution, crystallises from alcohol in colourless needles and melts at 144°.

2 : 5-*Dimethoxybenzophenone dichloride* (2 : 5-*dimethoxydiphenyldichloromethane*), $C_6H_3(OMe)_2{\cdot}CPhCl_2$, is formed by the action of phosphorus pentachloride on 2 : 5-dimethoxybenzophenone on the water-bath; it crystallises in colourless prisms, decomposes gradually on exposure to air, is moderately stable towards cold water, but is hydrolysed rapidly by boiling water, and gives an intense green coloration with aluminium chloride in benzene solution. When heated with aniline, it forms 2 : 5-*dimethoxybenzophenonephenylimine*, $CPh(OMe)_2{\cdot}C_6H_3{:}NPh$, which crystallises from alcohol in long, lemon-yellow needles, melts at 146°, and is hydrolysed by cold dilute hydrochloric acid, with formation of aniline and dimethoxybenzophenone.

4′-*Dimethylamino*-2 : 5-*dimethoxytriphenylmethane*,

$$C_6H_3(OMe)_2{\cdot}CHPh{\cdot}C_6H_4{\cdot}NMe_2,$$

is prepared by heating 2 : 5-dimethoxybenzophenone dichloride with dimethylaniline on the water-bath; it separates from alcohol in colourless crystals, melts at 112°, and is soluble in dilute mineral acids.

When reduced with zinc dust in boiling glacial acetic acid solution, 2 : 5-dimethoxybenzophenone yields the *pinacone*,

$$C_6H_3(OMe)_2{\cdot}CPh(OH){\cdot}CPh(OH){\cdot}C_6H_3(OMe)_2,$$

which crystallises in long, glistening, silky needles and melts at 162°.

2 : 5-*Dimethoxydiphenylethylcarbinol*, $C_6H_3(OMe)_2{\cdot}CEtPh{\cdot}OH$, is prepared by the action of dimethoxybenzophenone on magnesium ethyl bromide and treatment of the product with ice-water; it separates from light petroleum in large, transparent crystals, melts at 56°, boils at 230° under 30 mm. pressure, is readily soluble in ether, chloroform, carbon disulphide, acetone, glacial acetic acid, or benzene, gives a dark blue coloration with concentrated sulphuric acid or phosphoric acid, and when boiled with 60 per cent. sulphuric acid decomposes and forms a solution with violet fluorescence. When treated with hydrogen chloride in ethereal solution cooled by ice, the carbinol yields the *chloride* as an oily liquid, which, when heated on the water-bath, loses hydrogen chloride and forms 2 : 5-*dimethoxy-αα-diphenylpropylene*, $C_6H_3(OMe)_2{\cdot}CPh{:}CHMe$; this is formed also by boiling the carbinol with acetyl chloride in benzene solution in a reflux apparatus. It is a liquid which boils at 198° under 12 mm. pressure, gives a bluish-violet coloration with concentrated sulphuric acid, and decomposes, forming a solution with intense violet fluorescence, when boiled with 60 per cent. sulphuric acid. With bromine in chloroform solution, it forms an unstable *dibromide*, which on evaporation loses hydrogen bromide and yields the *bromo*-derivative,

$$C_6H_3(OMe)_2{\cdot}CPh{:}CMeBr;$$

this crystallises from light petroleum and melts at 81·5°.

2 : 5-*Dimethoxydiphenylmethylcarbinol*, $C_6H_3(OMe)_2{\cdot}CPhMe{\cdot}OH$, is

prepared in the same way as the ethylcarbinol; it separates from light petroleum in transparent crystals, melts at 65°, is readily soluble in most solvents, and gives a blue coloration with concentrated sulphuric acid. When treated with hydrogen chloride, it yields 2 : 5-*dimethoxy-α-phenylstyrene*, $C_6H_3(OMe)_2\cdot CPh{:}CH_2$, which is obtained as a light yellow oil boiling at 206—207° under 21 mm. pressure. It dissolves in benzene or acetone, forming a solution with slight fluorescence, and with bromine in chloroform solution forms a *dibromide* which readily loses hydrogen bromide.

2 : 5-*Dimethoxydiphenylbenzylcarbinol*,

$$C_6H_3(OMe)_2\cdot CPh(CH_2Ph)\cdot OH,$$

crystallises from alcohol in long, white needles, melts at 110°, is readily soluble in carbon disulphide, chloroform, or benzene, and gives a greenish-brown coloration with concentrated sulphuric acid.

2 : 5-*Dimethoxyphenylstilbene*, $C_6H_3(OMe)_2\cdot CPh{:}CHPh$, separates from light petroleum in large, white crystals, melts at 82·5°, and is sparingly soluble in alcohol or light petroleum, but is readily so in the other ordinary solvents. It unites with bromine to form a *dibromide*, which readily loses hydrogen bromide, forming the *bromo*-derivative, $C_6H_3(OMe)_2\cdot CPh{:}CPhBr$; this crystallises from a mixture of benzene and light petroleum and melts at 118°.

2 : 5-*Dimethoxytriphenylcarbinol*, $C_6H_3(OMe)_2\cdot CPh_2\cdot OH$, is prepared by the action of magnesium phenyl bromide on dimethoxybenzophenone or on ethyl 2 : 5-dimethoxybenzoate; it crystallises from alcohol, melts at 141°, is readily soluble in chloroform, benzene, or glacial acetic acid, and gives an emerald-green coloration with concentrated sulphuric acid. If a current of hydrogen chloride is passed through a solution of the carbinol in benzene containing anhydrous sodium sulphate, there is formed 2 : 5-dimethoxytriphenylmethyl chloride, $C_{21}H_{19}O_2Cl$, which crystallises in white needles and melts at 98°. When boiled with sodium ethoxide in absolute alcoholic solution, the chloride forms the *ethyl ether* of the carbinol,

$$C_6H_3(OMe)_2\cdot CPh_2\cdot OEt,$$

which separates from alcohol in large, white crystals, melts at 85—86°, and dissolves in concentrated sulphuric acid, forming an emerald-green solution.

2 : 5-*Dimethoxytriphenylmethane*, $C_6H_3(OMe)_2\cdot CHPh_2$, is formed by boiling the carbinol or its chloride or ethyl ether with hydrogen chloride in alcoholic solution, or by reducing the carbinol with zinc dust and boiling glacial acetic acid; it crystallises from alcohol in white needles melting at 104°, or from the super-cooled, concentrated alcoholic solution in leaflets melting at 84°, and gives a yellow coloration with concentrated sulphuric acid.

The *dimethyl ether* of phenylacetylquinol (2 : 5-*dimethoxydeoxybenzoin*), $C_6H_3(OMe)_2\cdot CO\cdot CH_2Ph$, is formed together with a small quantity of the *monomethyl ether* by the action of phenylacetyl chloride and aluminium chloride on *p*-dimethoxybenzene in cooled carbon disulphide solution; it separates from light petroleum in light yellow crystals, melts at 49°, boils at 226—227° under 16 mm. pressure, gives an intense orange coloration with concentrated sulphuric acid, and dissolves in *iso*butyl alcohol forming a solution with violet-blue, in benzyl alcohol forming a solution with a less intense blue, and in ethyl or methyl alcohol forming a solution with slight blue, fluorescence.

The *phenylhydrazone* forms an oil. The ketone interacts with magnesium phenyl bromide, forming 2 : 5-dimethoxydiphenylbenzylcarbinol, melting at 110°.

2 : 5-*Dimethoxy-a-benzylstilbene*, $C_6H_3(OMe)_2\cdot C(CH_2Ph){:}CHPh$, formed by the action of magnesium benzyl chloride on 2 : 5-dimethoxydeoxybenzoin, is a viscid, yellow oil, which boils at 278° under 15 mm. pressure, dissolves in the usual solvents, forming solutions with violet or blue fluorescence, and with bromine forms slowly an *additive* compound, losing hydrogen bromide at the laboratory temperature.

2 : 5-*Dimethoxypalmitylbenzene*, $C_6H_3(OMe)_2\cdot CO\cdot C_{15}H_{31}$, formed by the action of palmityl chloride and aluminium chloride on *p*-dimethoxybenzene in carbon disulphide solution, separates from alcohol in white crystals, melts at 44°, gives an orange coloration with concentrated sulphuric acid, and dissolves in ethyl or *iso*butyl alcohol forming a solution with violet, in methyl or benzyl alcohol forming a solution with weak blue, fluorescence.

The *phenylhydrazone*, $C_{30}H_{46}O_2N_2$, separates from alcohol in white crystals, becomes brown when exposed to air, melts at 64°, and forms solutions which are not fluorescent.

Ethyl 2 : 5-*dimethoxyphenylglyoxylate*, $C_6H_3(OMe)_2\cdot CO\cdot CO_2Et$, formed from ethoxalyl chloride and *p*-dimethoxybenzene, crystallises from light petroleum in slightly yellow leaflets, melts at 38°, boils at 200° under 11 mm. pressure, and is readily soluble in the usual solvents, forming yellow solutions in alcohol and glacial acetic acid.

2 : 5-*Dimethoxybenzamide*, $C_6H_3(OMe)_2\cdot CO\cdot NH_2$, is formed by the action of carbamic chloride and aluminium chloride on *p*-dimethoxybenzene in carbon disulphide solution; it crystallises from water in long, glistening needles, melts at 140°, is readily soluble in benzene, chloroform, acetone, or boiling water, and gives a coloration with concentrated sulphuric acid; the alcoholic, glacial acetic acid, and aqueous solutions have a violet fluorescence. The *nitrile*,

$$C_6H_3(OMe)_2\cdot CN,$$

formed by heating the amide with phosphorus pentachloride on the water-bath, crystallises from alcohol in white needles, melts at 82°, and has a slight violet fluorescence in alcoholic or glacial acetic acid solution.

Dicyanodimethoxybenzene, $C_{10}H_8O_2N_2$, is formed by the action of an excess of methyl sulphate and aqueous sodium hydroxide on dicyanoquinol (Thiele and Meisenheimer, Abstr., 1900, i, 299); it crystallises from alcohol in slightly yellow needles, melts at 280—281°, is only sparingly soluble in the usual solvents, and when dissolved in alcohol or glacial acetic acid has an intense violet, in acetone or benzene a weaker violet, fluorescence. The luminescence of dicyanoquinol is greatly increased by the methylation of the two hydroxyl groups.

2 : 5-Dimethoxybenzoic acid (Tiemann and Müller, Abstr., 1882, 52), formed by hydrolysis of its amide, dissolves in glacial acetic acid or alcohol, forming a solution having an intense violet fluorescence; the aqueous solution has a violet fluorescence which is diminished by addition

of an alkali hydroxide. The *ethyl* ester, $C_6H_3(OMe)_2\cdot CO_2Et$, formed by the action of hydrogen chloride on the acid in alcoholic solution, is a colourless liquid which boils at 167—168° under 14 mm. or at 285° under the atmospheric pressure, has the sp. gr. 1·1443 at 26°/26°, and when dissolved in alcohol or glacial acetic acid has an intense, in other solvents a weaker, violet fluorescence; it gives a blue luminescence when acted on by the Tesla rays. The ester interacts with magnesium phenyl bromide to form 2 : 5-dimethoxytriphenylcarbinol.

2 : 5 : 2′ : 5′-*Tetramethoxybenzophenone*, $CO[C_6H_3(OMe)_2]_2$, is formed by the successive action of phosphorus pentachloride and of *p*-dimethoxybenzene and aluminium chloride on 2 : 5-dimethoxybenzoic acid in carbon disulphide solution; it separates from alcohol in slightly yellow crystals, melts at 109°, is readily soluble in benzene, chloroform, or acetone, forms a yellow solution in alcohol or glacial acetic acid, and gives a coloration with concentrated sulphuric acid, but is not fluorescent. The *phenylhydrazone*, $C_{23}H_{24}O_4N_2$, forms white crystals and melts at 170°. The *oxime*, $C_{17}H_{19}O_5N$, is colourless, melts at 134·5°, and when treated with phosphorus pentachloride in ethereal solution is converted into 2 : 5-*dimethoxybenzoyl*-2 : 5-*dimethoxyanilide*, $C_6H_3(OMe)_2\cdot CO\cdot NH\cdot C_6H_3(OMe)_2$. This crystallises in white needles, melts at 120°, and is not fluorescent (compare Bargellini, Abstr., 1905, i, 210).

The action of 2 : 5 : 2′ : 5′-tetramethoxybenzophenone on magnesium ethyl bromide leads to the formation of 2 : 5 : 2′ : 5′-*tetramethoxydiphenylethylcarbinol*, $CEt[C_6H_3(OMe)_2]_2\cdot OH$, which separates from light petroleum in colourless crystals, melts at 120°, is readily soluble in benzene, chloroform, or glacial acetic acid, and gives a blue coloration with concentrated sulphuric acid. When treated with hydrogen chloride in benzene solution in presence of calcium chloride, the carbinol yields 2 : 5 : 2′ : 5′-*tetramethoxy-αα-diphenylpropylene*,

$$CHMe:C[C_6H_3(OMe)_2]_2,$$

which melts at 87°, gives a blue coloration with concentrated sulphuric acid, and is slightly fluorescent in acetone solution; with bromine, it forms an unstable *additive* compound, which readily loses hydrogen bromide. G. Y.

Certain Derivatives of Tetrabromo-*o*-benzoquinone. C. Loring Jackson and Frederick W. Russe (*Amer. Chem. J.*, 1906, **35**, 154—187).—By the action of cold acetone on tetrabromo-*o*-benzoquinone, hexabromo-*o*-quinocatechol ether (Jackson and Koch, Abstr., 1901, i, 597), hexabromo-*o*-dihydroxycatechol ether (*loc. cit.*), and heptabromo-*o*-quinocatechol hemiether are produced. Any of these substances can be obtained as the chief product of the reaction by careful adjustment of the conditions.

Heptabromo-o-quinocatechol hemiether, $OH\cdot C_6Br_4\cdot O\cdot C_6Br_3O_2$, crystallises from benzene in large, square, yellow plates or prisms which effloresce on exposure to the air; it darkens between 200° and 240°, melts and decomposes at 244—245°, and is soluble in hot benzene, chloroform, ether, or nitrobenzene. The compound dissolves in ethyl alcohol, but, if the solution is warmed, decomposition occurs with formation of hexabromo-*o*-quinocatechol ether. When heptabromo-*o*-

quinocatechol hemiether is reduced with zinc and dilute acetic acid, hexabromodihydroxycatechol ether is produced. By the action of benzoyl chloride on the hemiether, *tribenzoylheptabromodihydroxycatechol hemiether*, $OBz \cdot C_6Br_4 \cdot O \cdot C_6Br_3(OBz)_2$, is obtained, which crystallises from benzene in small, flat, transparent plates, melts at 294—296°, and is soluble in benzene, sparingly so in alcohol, and insoluble in water.

When tetrabromo-*o*-benzoquinone is heated with benzoyl chloride, a compound is obtained which agrees in composition with tetrabromocatechol dibenzoate, but melts at 172—174° instead of 197°. *Tetrabromocatechol dibenzoate*, $C_6Br_4(OBz)_2$, obtained by heating tetrabromocatechol with benzoyl chloride for seven hours, crystallises in square, transparent plates, melts at 197°, and is soluble in benzene or chloroform and slightly so in alcohol. When tetrabromocatechol is heated with benzoyl chloride for only five to ten minutes, a compound is obtained which forms long, white needles, melts at 215—216°, and is probably impure tetrabromocatechol monobenzoate.

When tetrabromo-*o*-benzoquinone is left in contact with acetophenone, the same three products are obtained as are formed by the action of acetone, together with some ω-bromoacetophenone. Diethyl ketone and mesityl oxide react with the quinone in a similar manner. When a few drops of bromine are added to a mixture of acetone and tetrabromo-*o*-benzoquinone, hexabromo-*o*-quinocatechol ether and heptabromo-*o*-quinocatechol hemiether are produced, but very little of the hexabromodihydroxycatechol ether is formed. In corresponding experiments with hexabromo-*o* quinocatechol ether, the dihydroxy-compound is obtained in brown plates and also in white, fibrous needles, and it is proved that the two products are identical in spite of the difference in their appearance.

When tetrabromo-*o*-benzoquinone is treated with heptaldehyde or benzaldehyde, hexabromo-*o*-quinocatechol ether and heptabromo-*o*-quinocatechol hemiether are produced.

By the action of tetrabromocatechol on tetrabromo-*o*-benzoquinone, Zincke (Abstr., 1887, 808) obtained a black compound which he did not study closely. This compound is now found to be *octabromo-*o*-quinhydrone*, $C_6Br_4O_2,C_6Br_4(OH)_2,H_2O$; it crystallises in lustrous, black needles or slender prisms, and is soluble in ether, chloroform, or benzene, and insoluble in water. The quinhydrone cannot be purified by crystallisation from benzene, as in this solvent the substance gradually decomposes into heptabromo-*o*-quinocatechol hemiether and tetrabromocatechol. The decomposition of the compound with boiling benzene takes place according to the equation:

$$3[C_6Br_4O_2,C_6Br_4(OH)_2,H_2O] = 2C_{12}HO_4Br_7 + 2C_6Br_4(OH)_2 + Br_2 + 3H_2O.$$

The same change takes place when the dry substance is heated at 110°.

Tetrabromocatechol diacetate forms colourless plates, melts at 215—216°, and is soluble in chloroform, alcohol, benzene, or ether.

By the action of warm acetic acid on tetrabromo-*o*-benzoquinone, Jackson and Koch (Abstr., 1901, i, 598) obtained a white substance, $C_{14}H_2O_5Br_8$, which melted at 230°. Jackson and Porter (Abstr., 1904, i, 255) could not obtain this substance, but isolated a yellow product melting at 244—245°. Further attempts to prepare the substance described by Jackson and Koch have resulted in the formation of hexabromo-*o*-quinocatechol ether. In one experiment, a yellow, crystalline substance melting at 235—250° was obtained, whilst in another experiment, in which the tetrabromo-*o*-benzoquinone was heated for a longer time with acetic acid at 100°, heptabromo-*o*-quinocatechol hemiether was produced.

When tetrabromo-*o*-benzoquinone is left in contact with glacial acetic acid at the ordinary temperature, the additive *compound*,

$$2C_6O_2Br_4,3CH_3\cdot CO_2H,$$

is obtained, which crystallises in white, rhombic plates, gradually becomes red when heated, but does not melt below 300°, and is soluble in alcohol, ether, benzene, or chloroform. On repeated crystallisation from benzene, the substance is converted into the yellow compound, melting at 235—250°, which was obtained by the action of hot acetic acid, and is probably *diheptabromo*-o-*quinocatechol ether*,

$$O(C_6Br_4\cdot O\cdot C_6Br_3O_2)_2;$$

this substance is also formed by the action of formic acid on tetrabromo-*o*-benzoquinone. Propionic acid, butyric acid, and *iso*valeric acid seem to react with tetrabromo-*o*-quinone with formation of the same compound.

An attempt was made to prepare an additive compound of tetrabromo-*o*-benzoquinone with bromine, but without success. On heating the quinone with fuming nitric acid and bromine, two compounds were obtained, one yellow, the other white. The yellow substance, which is probably *tetrabromo*cyclo*pentene*-o-*quinone*,  $CBr<\begin{matrix}CBr\text{--}CO\\ CBr_2\cdot CO\end{matrix}$, crystallises in plates or prisms, melts at 142°, is soluble in alcohol, ether, chloroform, benzene, or acetone, and when treated with *o*-diamines gives a deep red colour characteristic of quinoxalines of this class. The white *compound* crystallises in needles, melts at 144—146°, is very soluble in water, and has an acid reaction.

By the action of *o*-phenylenediamine or 4:6-dibromo-*o*-phenylenediamine on tetrabromo-*o*-benzoquinone, a dark red, amorphous product is formed. When tetrabromo-*o*-benzoquinone is treated with potassium phenoxide or sodium alkyloxides, brown or red amorphous products are obtained.
E. G.

1:4-Anthraquinone. HANS DIENEL (*Ber.*, 1906, **39**, 926—933. Compare Abstr., 1905, i, 767).—2-*Nitroso*-1-*anthrol*.—The *zinc* salt, $(O:C_{14}H_8:N\cdot O)_2Zn$, obtained by heating an alcoholic solution of 1-anthrol with sodium nitrite and a concentrated aqueous solution of zinc chloride, is a dark red, crystalline powder. By the action of a hot dilute solution of sodium hydroxide, 2-nitroso-1-anthrol is prepared. It crystallises in reddish-brown or orange needles, decomposes at about 200°, and develops a violet-red colour with concentrated sulphuric acid. The *potassium* salt crystallises in yellow needles or leaflets and is decomposed by water. The *ethyl ether*, $O:C_{14}H_8:N\cdot OEt$, obtained from the silver salt and ethyl iodide, crystallises in glistening, yellow needles and melts at 144°. The *methyl ether* melts at 134°. 2-*Amino*-1-*anthrol hydrochloride* is obtained by the reduction of 2-nitroso-1-anthrol or its salts by stannous chloride and hydrochloric acid; it readily oxidises in the air, and by acetylation yields *triacetyl-2-amino-1-anthrol*, $OAc{\cdot}C_{14}H_8{\cdot}NAc_2$, which crystallises in glistening, green leaflets or needles and melts at 161°. Each of the two compounds just mentioned is readily oxidised to 1 : 2-anthraquinone by ferric chloride in the presence of hydrochloric acid.

4-*Nitroso-1-anthrol* separates after some time from the reddish-brown mother liquor from which the zinc salt of 2-nitroso-1-anthrol is obtained; it forms glistening, brown needles, which darken at 205° and melt and decompose at 233°. The *potassium* and *sodium* salts are yellowish-brown substances which are readily decomposed by water or alcohol. 4-Nitroso-1-anthrol dissolves in concentrated sulphuric acid with a characteristic indigo-blue coloration.

1 : 4-*Anthraquinone* is obtained by the reduction of 4-nitroso-1-anthrol, followed by the oxidation of the stannochloride so produced with ferric chloride. It crystallises in long, yellow needles, melts at 206°, readily sublimes, and is volatile in steam. Its constitution is proved by simultaneous reduction and acetylation to diacetyl-1 : 4-anthraquinol, from which diacetylquinizarin is obtained by oxidation with chromic and acetic acids. The last compound is hydrolysed to quinizarin by alcoholic potassium hydroxide.

Anthracene-1-nitrile, obtained by distilling a mixture of anthracene-1-sulphonate with powdered potassium cyanide, crystallises in glassy, yellow leaflets and melts at 126°.

Anthraquinone-1-nitrile, $C_{14}H_7O_2{\cdot}CN$, obtained by the oxidation of the preceding compound or by the distillation of anthraquinone-1-sulphonate and potassium cyanide, crystallises in golden-yellow leaflets and melts at 216—217°. After prolonged hydrolysis, these two nitriles are converted into the corresponding acids. *Anthracene-1-carboxylic chloride*, $C_{14}H_9{\cdot}COCl$, is stable in the presence of water. The *amide*, $C_{14}H_9{\cdot}CO{\cdot}NH_2$, obtained by passing ammonia into a benzene solution of the chloride, crystallises in colourless needles or leaflets and melts at 256°. *Anthraquinone-1-carboxylamide* melts at 260°. C. S.

Diaminoanthraquinones. EMILIO NOELTING and W. WORTMANN (*Ber.*, 1906, **39**, 637—646).—The mixture of amines obtained by boiling gently Römer's mixed dinitroanthraquinones (Abstr., 1883, 737) with aqueous sodium sulphide for some hours is boiled with dilute sulphuric acid and filtered. The insoluble sulphate, after recrystallisation from moderately concentrated sulphuric acid, yields Römer's 1 : 5-diaminoanthraquinone melting at 319° (*loc. cit.*); it dissolves in boiling dilute oxalic acid and crystallises out unchanged on cooling. 1 : 5-Dibenzoylaminoanthraquinone, $C_{14}H_6O_2(NHBz)_2$, formed by boiling Römer's base with benzoyl chloride and dimethylaniline, melts above 350°.

The bases present in the sulphuric acid filtrate from the sulphate of Römer's base are precipitated by dilution with much water and converted into their acetyl derivatives by boiling with acetic anhydride and acetic acid, when on cooling there crystallises out 1 : 8-*diacetylaminoanthraquinone*, $C_{14}H_6O_2(NHAc)_2$, which forms brownish-yellow needles and melts at 284°; the more soluble isomerides remain in solution. 1 : 8-*Diaminoanthraquinone*, $C_{14}H_6O_2(NH_2)_2$, obtained by treating the diacetyl derivative with ammonia or by heating anthraquinone-1 : 8 disulphonic acid with ammonia, crystallises from alcohol, glacial acetic acid, nitrobenzene, or pyridine, melts at 262°, is more readily soluble than the 1 : 5-isomeride, and has feeble basic properties. The *sulphate*, $C_{14}H_6O_2(NH_2)_2,H_2SO_4$, crystallises in glistening, black needles; the *hydrochloride*, $C_{14}H_6O_2(NH_2)_2,HCl$, forms a reddish-brown, amorphous mass. 1 : 8-*Dibenzoylaminoanthraquinone*, $C_{14}H_6O_2(NHBz)_2$, crystallises in glistening, yellow needles and melts at 324°. The *diacetyl* derivative melts at 284°.

When treated in the above manner, Böttger and Petersen's α-diaminoanthraquinone melting at 236° (this Journal, 1873, **26**, 389) is found to be a mixture of 1 : 5- and 1 : 8-diaminoanthraquinones, together with isomerides forming more soluble acetyl derivatives.

2 : 7-Diaminoanthraquinone (β-diaminoanthraquinone : Schmidt, this Journal, 1874, **27**, 987), formed by reduction of β-dinitroanthraquinone with sodium sulphide, crystallises from nitrobenzene or alcohol in orange-yellow needles and melts above 330°. The *sulphate*,

$$C_{14}H_6O_2(NH_2)_2,H_2SO_4,$$

crystallises in colourless needles, becomes red on exposure to air, and is hydrolysed by much water; the *hydrochloride*, $C_{14}H_6O_2(NH_2)_2,HCl$, was analysed; the *diacetyl* derivative, $C_{14}H_6O_2(NHAc)_2$, crystallises from nitrobenzene and melts above 350°. When diazotised and coupled with α-naphtholsulphonic acid, the 2 : 7-diamine forms a *derivative*, which dyes cotton wool directly but not intensely; when treated with nitrosyl sulphate in sulphuric acid solution and boiled with water, the diamine forms *iso*anthraflavic acid. *Methyl* iso*anthraflavate*, formed by the action of methyl sulphate and potassium hydroxide on the acid, crystallises from glacial acetic acid and melts at 214°.

When heated with oxalic acid at 150—160°, 1-aminoanthraquinone forms the *oxamic acid*, $C_{14}H_7O_2{\cdot}NH{\cdot}C_2O_3H$, which melts at 226°, and, when treated with nitric acid in sulphuric acid solution, yields 4-nitro-1-aminoanthraquinone (D.R.-P. 125391; Abstr., 1902, i, 382) melting at 296°. On reduction with sodium sulphide, it yields 1 : 4-*diaminoanthraquinone*, $C_{14}H_6O_2(NH_2)_2$, which crystallises from alcohol, melts at 268°, and dissolves in sulphuric or hydrochloric acid, forming a red solution. 1 : 4-*Diacetylaminoanthraquinone*, $C_{14}H_6O_2(NHAc)_2$, forms reddish-yellow needles and melts at 271°.

When heated with oxalic acid at 150—160°, 1 : 5-diaminoanthraquinone forms the *dioxamic acid*, $C_{14}H_6O_2(NH{\cdot}C_2O_3H)_2,2H_2O$, which is obtained as a yellow powder; it loses $2H_2O$ at 140—150°, becomes red at 250°, and decomposes at about 300° (D.R.-P. 158076); on nitration in sulphuric acid solution, it yields 4 : 8-dinitro-1 : 5-diaminoanthraquinone (Abstr., 1902, i, 476). This is reduced by sodium sulphide, forming 1 : 4 : 5 : 8-tetra-aminoanthraquinone, which melts at 332°, and, in dilute acetic acid solution, dyes cotton wool mordanted with tannin, but not silk, violet-blue; after treatment with methyl sulphate and sodium acetate in acetic acid solution, it dyes silk moderately, or cotton wool mordanted with tannin an intense, blue. A diagram is given showing the results of the spectroscopic examination of the tetra-amino-compound.

With pyridine, the tetra-amino base forms the *additive* compound,

$$C_{11}H_4O_2(NH_2)_4,C_5NH_5,$$

which crystallises in red needles; the *sulphate*,

$$C_{11}H_4O_2(NH_2)_4,2H_2SO_4,$$

crystallises in needles; the *tetra-acetyl* derivative, $C_{11}H_4O_2(NHAc)_4$, forms orange-red needles or thick, green, shimmering crystals, and melts above 330°.

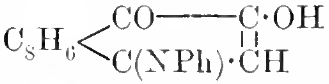
When boiled with chlorodinitrobenzene and sodium acetate in alcoholic solution in a reflux apparatus, the tetra-amino compound yields the *product*, $C_{11}H_4O_2(NH_2)_3\cdot NH\cdot C_6H_3(NO_2)_2$, which crystallises in green, shimmering needles and does not melt at 340°. G. Y.

Blue and Green Anthracene Dyes. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 159129).—4-Bromo-1-methylaminoanthraquinone condenses with *p*-toluidine on boiling, and on cooling to 60° and adding methyl alcohol, dark blue crystals with coppery lustre of 4 *p-toluidino-1-methylaminoanthraquinone* separate. The product dissolves in chloroform or pyridine to bluish-green solutions. Aniline, *o*-toluidine, xylidine, or naphthylamine may replace the *p*-toluidine. Similar compounds are obtained from 4-bromo-1-methylamino-2-methylanthraquinone, dibromo-1 : 5-dimethyldiaminoanthraquinone or 4-bromo-1-methylaminoanthraquinonesulphonic acid. C. H. D.

Preparation of Aminohydroxyanthraquinonesulphonic Acids. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 161035).—When *p*-aminohydroxyanthraquinone or its alkyl derivatives are sulphonated, the sulpho-group enters the ring containing the amino- and hydroxy-groups. When, however, the boric esters are sulphonated, or when sulphonation is carried out in the presence of boric acid, heteronucleal sulphonic acids are obtained. The reaction takes place at 110—120°.

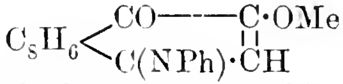
Unlike the homonucleal sulphonic acids, the products give characteristic colorations when boric acid is added to their solutions in concentrated sulphuric acid. C. H. D.

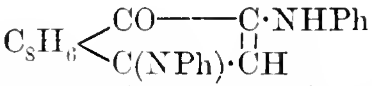
Compounds of Aniline with 1 : 2-Anthraquinone and a New Hydroxyanthraquinone. Kasimir Lagodzinski (*Annalen*, 1906, **344**, 78—92. Compare this vol., i, 98; Kehrmann, Abstr., 1898, i, 439).—1 : 2-Anthraquinone dissolves in aniline at the laboratory temperature with development of heat and formation of 2-*hydroxy*-1 : 4-*anthraquinone*-4-*anil*,

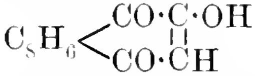


$$C_8H_6<\begin{matrix}CO\text{———}C\cdot OH\\ \quad\quad\quad\quad\ \ \| \\ C(NPh)\cdot CH\end{matrix}$$

, together with a small quantity of 2-anilino-1 : 4-anthraquinone-4-anil, which is removed by washing the product with alcohol and warm benzene. The anil, purified by solution in warm alcoholic potassium hydroxide, precipitation with acetic acid, and recrystallisation from benzene, forms matted, thin, glistening, fiery-red needles containing C_6H_6, decomposes at about 255°, dissolves in concentrated sulphuric acid forming a brownish-red solution, is readily soluble in aqueous or alcoholic alkali hydroxides, and forms orange-yellow *alkali* salts. On reduction with glacial acetic acid and zinc dust, the anilide forms a greenish-yellow solution which becomes reddish-brown when shaken with air, but if the reduction is effected with an excess of zinc dust and prolonged warming, a stable, dark green solution is obtained. On oxidation with a dilute solution of chromic acid in glacial acetic acid solution, the anil yields a *product* which separates in colourless crystals. The *additive* compound, $C_{20}H_{13}O_2N,C_2H_4O$, formed when the anil is heated with glacial acetic acid, crystallises in long, scarlet needles, does not melt at 250°, and dissolves on warming in dilute alkali hydroxides, forming orange-yellow solutions.

2-*Methoxy*-1 : 4-*anthraquinone*-4-*anil*,  $C_8H_6<\begin{matrix}CO\text{——}C\cdot OMe\\ C(NPh)\cdot CH\end{matrix}$, formed by the action of methyl sulphate on the hydroxy-compound in alcoholic potassium hydroxide solution, crystallises in long, golden-yellow needles, melts at 175°, and is insoluble in aqueous alkali hydroxides, but dissolves in concentrated sulphuric acid, forming a brownish-red solution.

2-*Anilino*-1 : 4-*anthraquinone*-4-*anil*,  $C_8H_6<\begin{matrix}CO\text{——}C\cdot NHPh\\ C(NPh)\cdot CH\end{matrix}$, is formed by warming 1 : 2-anthraquinone or 2-hydroxy-1 : 4-anthraquinone-4-anil with an excess of aniline on the water-bath; it crystallises from benzene in matted, fiery-red needles, melts at 230°, is soluble in alcohol or glacial acetic acid, and dissolves in concentrated sulphuric acid, forming an intense rosaniline-red solution. When warmed with zinc dust and glacial acetic acid, it is reduced to the greenish-yellow leuco-base, which is oxidised by air.

2-Hydroxy-1 : 4-anthraquinone,  $C_8H_6<\begin{matrix}CO\cdot C\cdot OH\\ CO\cdot CH\end{matrix}$, is formed by heating finely-divided 2-hydroxy-1 : 4-anthraquinone-4-anil with equal volumes of concentrated hydrochloric acid and water in a sealed tube at 140—150° for one hour; it crystallises from alcohol in long, thin, dark yellow or light brown needles, becomes brown at 230°, decomposes at about 235°, sublimes almost undecomposed in small, sulphur-yellow needles, and dissolves in aqueous alkali hydroxides or carbonates, or in concentrated sulphuric acid forming a red solution. The *alkali* salts are orange-yellow; with barium and calcium chlorides, the ammoniacal solution forms voluminous, orange-yellow *precipitates*; the *silver* salt is obtained as a reddish-yellow precipitate which, when warmed with an excess of ammonia, forms a characteristic silver mirror. 2-*Acetoxy*-1 : 4-*anthraquinone*, $C_{16}H_{10}O_2$, crystallises in light-yellow leaflets or sulphur-yellow needles and melts at 188°. G. Y.

Preparation of 1 : 4 : 8-Trihydroxyanthraquinone. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 161026).—When the method employed for the conversion of alizarin into 1 : 2 : 5-trihydroxyanthraquinone (Abstr., 1905, i, 532) is applied to chrysazin, 1 : 4 : 8-trihydroxyanthraquinone is obtained. The oxidation is carried out with sulphuric acid containing 80 per cent. anhydride and boric acid at 25—35°. In the absence of boric acid, higher oxidation products, up to the hexahydroxy-compound, are obtained. Anthrarufin and quinizarin do not yield *a*-hydroxy-derivatives on similar treatment.

1 : 4 : 8-Trihydroxyanthraquinone separates from pyridine or nitrobenzene in brownish-red needles or leaflets with green reflex and dissolves in sodium hydroxide or concentrated sulphuric acid to violet solutions. C. H. D.

Presence of Guaiol in an Odoriferous Wood from New Guinea. P. A. A. F. Eyken (*Rec. trav. chim.*, 1906, **25**, 40—43).—This wood, which has the vernacular name "Kajoe garoe," yields, on distillation with steam, an essential oil which is nearly solid at the ordinary temperature. The product obtained by exposing the oil on a filter paper and recrystallising the residue from alcohol forms brilliant, long prisms, melts at 93°, has $[\alpha]_D$ − 30° at 17°, boils at 288—289°, and is identical with guaiol obtained from guaiacum wood (*Schimmel & Co.'s Berichte*, 1902, **1**, 42; compare Wallach and Tuttle, Abstr., 1894, i, 538). The crude oil, on distillation, yields formic and acetic acids and guaiol, and leaves a brown residue. If the oil is freed from acid and resinous matters by shaking its solution in ether with an alkali, it deposits guaiol after a time and leaves an oily liquid, which is dextrorotatory and is not separable into its constituents by fractional distillation. The botanical origin of the wood is unknown, but it appears to be derived from a conifer. T. A. H.

Pure Nerol. Hugo von Soden and Walter Treff (*Ber.*, 1906, **39**, 906—914).—Crude nerol, obtained from oil of petit-grain, is converted into the diphenylurethane derivative (compare H. and E. Erdmann, Abstr., 1898, i, 35), and the mixture of neryl- and geranyl-diphenylurethanes is separated almost completely by fractional crystallisation from light petroleum (b. p. 30—40°) or methyl alcohol, in which the latter is much less soluble. In this way it is shown that nerol, which has been freed from geraniol as completely as possible by treatment with calcium chloride, still contains 25 to 30 per cent. of that substance.

From *d*- or *l*-linalool, nerol has been isolated in the form of its pure diphenylurethane which melts at 52—53° (compare Hesse and Zeitschel, Abstr., 1903, i, 189). The action of acetic anhydride on linalool (*Chem. Ind.*, 1906, **29**, 20) yields nerol which contains geraniol.

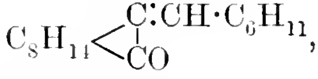
Pure nerol, prepared from the diphenylurethane by the action of an alcoholic solution of potassium hydroxide, is a colourless oil with the odour of roses; it boils at 125° under 25 mm. or at 224—225° under 755 mm. pressure, has a sp. gr. 0·8813 at 15°, and is optically inactive. The pure acetate boils at 93—94° under 3 mm. pressure, has the sp. gr. 0·916 at 15°, and the saponification number 286·2; the formate has not been obtained pure (compare Soden and Zeitschel, Abstr., 1903, i, 267). The *tetrabromide*, $C_{10}H_{18}OBr_4$, crystallises in long needles and melts at 118—119°.

A dilute solution of chromic acid oxidises nerol to an aldehyde which is apparently citral *b*.

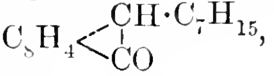
Pure geraniol boils at 229—230° under atmospheric pressure and at 94° under 3 mm., has the sp. gr. 0·8825 at 15°, and is optically inactive. The tetrabromide, $C_{10}H_{18}OBr_4$, crystallises in small needles and melts at 70—71°. C. S.

Rotatory Powers of Hexahydrobenzylidenecamphor and Œnanthylidenecamphor and the Corresponding Saturated Derivatives; Comparison of the Rotatory Powers of these Compounds with those of Benzylidenecamphor and Benzylcamphor.

Albin Haller and François March (*Compt. rend.*, 1906, **142**. 316—319. Compare Abstr., 1899, i, 770; ii, 622; 1900, i, 182; 1903, i, 503, 563, 628; 1904, i, 751; 1905, i, 602).

Hexahydrobenzylidenecamphor,  $C_8H_{14}{<}\genfrac{}{}{0pt}{}{C{:}CH\cdot C_6H_{11}}{CO}$, obtained by the action of hexahydrobenzaldehyde on the sodium derivative of camphor (Abstr., 1904, i, 600; 1905, i, 214), forms large, colourless crystals, which melt at 49°; it is readily soluble in ether or light petroleum and insoluble in water, and yields on reduction with sodium amalgam in acid solution *hexahydrobenzylcamphor*,

$$C_8H_{14}{<}\genfrac{}{}{0pt}{}{CH\cdot CH_2\cdot C_6H_{11}}{CO},$$

in the form of a colourless oil boiling at 192° under 24 mm. pressure. *Heptylcamphor* (*œnanthylcamphor*),  $C_8H_4{<}\genfrac{}{}{0pt}{}{CH\cdot C_7H_{15}}{CO}$, prepared by the action of *n*-heptyl iodide on the sodium derivative of camphor in the presence of toluene, is a colourless oil boiling at 190° under 25 mm. pressure; it yields a bromo-derivative which, on boiling with diethylaniline, loses HBr and forms *heptylidenecamphor* (*œnanthylidenecamphor*),  $C_8H_4{<}\genfrac{}{}{0pt}{}{C{:}CH\cdot C_6H_{13}}{CO}$, a colourless oil boiling at 180—182° under 20 mm. pressure.

The specific rotations of these new camphor derivatives are given in the following table, in which is also included the corresponding constants of benzylidenecamphor and benzylcamphor for the purpose of comparison.

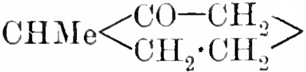
Rotatory Power of Unsaturated Series.	
Benzylidenecamphor	$[\alpha]_D$ +425°11′
Hexahydrobenzylidenecamphor	+131 39
Heptylidenecamphor	+136 40

Rotatory Power of Saturated Series.	
Benzylcamphor	$[\alpha]_D$ +144°00′
Hexahydrobenzylcamphor	+55 07
Heptylcamphor	+51 13

These numbers show (1) that the specific rotations of the new compounds are much lower than the specific rotations of the corresponding benzenoid compounds, (2) that the rotation of the saturated derivative is lower than that of the corresponding unsaturated compound, (3) that the cyclic or aliphatic nature of the group C_6H_{11} or C_6H_{13} does not appreciably modify the rotatory power in the two series. M. A. W.

Carvone Hydrate.

Emil Knoevenagel and Oskar Samel, *Ber.*, 1906, **39**, 677—685. Compare Rupe and Schlochoff, Abstr., 1905, i, 449).—Carvone hydrate (8-hydroxy-8 : 9-dihydrocarvone) is formed when carvone is boiled with 36·5 per cent. solution of sodium hydrogen sulphite until a clear solution is obtained, and the cold solution then treated with a mixture of equal parts of concentrated sulphuric acid and water, care being taken to avoid rise of temperature. After eight days, the carvone hydrate is precipitated by the addition of 25—30 per cent. sodium hydroxide solution. The yield is 80 per cent., and after crystallisation from a mixture of ether and light petroleum it melts at 42—43°.

When heated for three hours under reduced pressure, the hydrate is converted into carvacrol and carvone. It does not react with benzoyl chloride, phenylthiocarbimide, or hydrogen sulphide, nor does it yield a condensation product with benzaldehyde. The *phenylhydrazone*, $C_{16}H_{22}ON_2$, crystallises from alcohol in long, pale yellow needles and melts at 134—135°. The semicarbazone melts at 177—179° (Rupe and Schlochoff give 176°). When reduced with zinc dust in alkaline solution, the hydrate yields *dihydrocarvone hydrate* (8-*hydroxymenthan*-2-*one*),  $CHMe<\begin{matrix}CO-CH_2\\CH_2\cdot CH_2\end{matrix}>CMe_2\cdot OH$ (45 per cent. yield), which is also formed when Baeyer's glycol, dihydrocarveol hydrate (Abstr., 1895, i, 550), is oxidised with chromic acid in acetic acid solution. It distils at 138—139° under 9 mm. pressure, combines with sodium hydrogen sulphite, has a sp. gr. 1·006 at 19°/4°, n_D 1·476 at 20°, and $[\alpha]_D - 18·5°$ at 20°. The semicarbazone, $C_{11}H_{21}O_2N_3$, melts at 150·5—151°, whereas Baeyer and Henrich (*Ber.*, 1895, **28**, 1590) give 139° as the melting point.

Dehydrating agents convert carvone hydrate into carvacrol and carvone, but when the hydrate is heated for one hour with potassium hydrogen sulphate it is transformed quantitatively into carvacrol.

J. J. S.

Composition of the Volatile Oil of Backhousia citriodora from Queensland (*Bull. Imp. Inst.*, 1905, **3**, 11—13).—The volatile oil of *Backhousia citriodora* from Queensland is a greenish-yellow, transparent liquid, which has a strong odour of citral, a sp. gr. 0·8903 at 21°, n_D 1·4940 at 22°, and is optically inactive. It is miscible in all proportions with 80 per cent. alcohol, is completely soluble in 2·25 volumes of 70 per cent. alcohol, and contains 93·5 per cent. of citral. On distillation, 100 c.c. of the oil yields 10 c.c. boiling at 212—219°, 70 c.c. at 219—226°, and 10 c.c. at 226—231°.

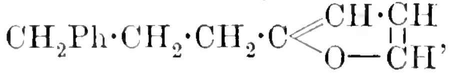
A specimen of the oil of *Backhousia citriodora*, examined previously (*Schimmel's Berichte*, 1888, part I, 20), was stated to have a sp. gr. 0·900 and to consist largely of citral.

E. G.

Composition of the Ethereal Oil of the Carline Thistle (Carlina acaulis L.). FRIEDRICH W. SEMMLER (*Ber.*, 1906, **39**, 726—731).—From the oil obtained by distillation of the dried roots of *Carlina acaulis* in a current of steam, the author had previously obtained the sesquiterpene, carlinene, $C_{15}H_{24}$, together with an oil containing oxygen and a crystalline solid (compare Gadamer, Abstr., 1903, i, 353).

The carlina oil yielded on fractional distillation 12—15 per cent. of carlinene, whilst palmitic acid was found in small amount. *Carlina oxide*, the principal constituent of the oil, was separated by repeated fractionation under diminished pressure; it boils at 167—168° under 20 mm. pressure, has a sp. gr. 1·066 at 17°/17° and n_D 1·586; it is optically inactive. Its probable formula is $C_{13}H_{10}O$. When oxidised by permanganate, it forms benzoic acid in large amount.

Tetrahydrocarlina oxide (*a-phenyl-γ-2-furylpropane*),



$$CH_2Ph\cdot CH_2\cdot CH_2\cdot C{<}\begin{matrix}CH\cdot CH\\ O-CH\end{matrix},$$

prepared by the reduction of carlina oxide with sodium and alcohol, is an oil which boils at about 135° under 10 mm. pressure and at about 262° (uncorr.) at the ordinary pressure. When oxidised by permanganate it is converted into *γ-phenyl-*n*-butyric acid*,

$$CH_2Ph\cdot CH_2\cdot CH_2\cdot CO_2H,$$

which crystallises in glistening leaflets, melts at 52°, and boils at about 165° under 10 mm. pressure; on further oxidation, this acid is converted into benzoic acid.

The presence of the furan ring in the molecule of tetrahydrocarlina oxide was shown by its synthesis from acetophenone and furfuraldehyde in the presence of alcoholic sodium ethoxide.

The conclusion is drawn that a furan ring, united with a phenyl group by a chain of three carbon atoms, is present in the molecule of carlina oxide. A. McK.

Essence of the Wood of Gonystylus miquelianus. P. A. A. F. Eyken (*Rec. trav. chim.*, 1906, **25**, 44—47).—The crude essence obtained by distilling the old wood in steam is a crystalline mass, melts at 66—68°, boils at 280—290°, and has $[a]_D+35°$ in alcohol. By repeated crystallisation from acetic acid or alcohol, a sesquiterpene alcohol, *gonystylol*, $C_{15}H_{26}O$, was isolated. This, after distillation under reduced pressure, forms silky crystals, melts at 82°, boils at 164—166° under 17 mm. pressure, and has $[a]_D+30°$ at 17° in alcohol. When heated with formic acid, it yields *gonystylene*, a colourless, mobile liquid, which boils at 137—139° under 17 mm. pressure, has a sp. gr. 0·9183 at 17°, $[a]_D+40°$ at 17° in alcohol, and n_D 1·5134 at 15° (indicating the presence of two ethylenic linkings). No bromide, hydrochloride, hydrobromide, or corresponding alcohol could be prepared from gonystylene by the usual methods. It is pointed out that gonystylol and gonystylene have respectively the same specific rotations as guaiol (see this vol., i, 295) and guaiene, but in the opposite sense. T. A. H.

Lemon-grass Oil from Montserrat (*Bull. Imp. Inst.*, 1904, **2**, 166—167).—The oil of *Andropogon nardus*, var. *genuinus*, from Montserrat, is a clear, limpid, yellow liquid, with a pleasant, lemon-grass odour, and is soluble in 70 per cent. alcohol to the extent of 97 per cent. On distillation, about 25 per cent. of the oil is obtained between 180° and 220°, and 50 per cent., consisting principally of citral, between 220° and 230°. The oil has a sp. gr. 0·906 at 15°, $a_D-0°10'$ in a 100 mm. tube, and contains 74·6 per cent. of citral.

A sample of the oil, examined in the West Indies, had a sp. gr.

0·886 at 15°, $\alpha_D - 0°12·6'$ in a 100 mm. tube, and contained 74·2 per cent. of citral.

A comparison of this West Indian oil with the lemon-grass oil obtained in India from *Andropogon citratus* shows that the former contains as much citral as the latter, from which it only differs in being incompletely soluble in 70 per cent. alcohol. E. G.

New Ethereal Oils. RICHARD SCHMIDT and KARL WEILINGER (*Ber.*, 1906, **39**, 652—658).—The oil from *Ocotea usambarensis* is limpid and of a yellow colour. It distils at 50—160° under 10 mm. pressure, some 75 per cent. passing over below 100°. It has a sp. gr. 0·913 at 20°, n_D 1·476, and $\alpha_D - 11°12'$ at 20°. It consists of myristaldehyde 1, cineol 40, *l*-terpineol 40, a *sesquiterpene*, $C_{15}H_{24}$ or $C_{15}H_{26}$, 10, esters 4 per cent., and a minute quantity of a *ketone* which yields a semicarbazone melting at 197°.

The oil from the leaves of *Piper volkensii* has a pale brown colour and an intense pleasant odour. It distils at 90—175° under 12 mm. pressure, has a sp. gr. 0·934 at 20°, n_D 1·5017, and $\alpha_D - 8°24'$. It contains 25 per cent. of limene (Burgess and Page, Trans., 1904, **85**, 414) and 45 per cent. of a *compound*, $C_{11}H_{12}O_3$, probably a methoxysafrole,


$C_3H_5{\cdot}C_6H_2(OMe)\left\langle\begin{matrix}O\\O\end{matrix}\right\rangle CH_2$, which distils at 136—140° under 12 mm. pressure, has a sp. gr. 1·137 at 20°, n_D 1·5416, but is optically inactive. Limene yields a *hexabromide*, $C_{15}H_{24}Br_6$, which crystallises from light petroleum and melts at 154°. The compound $C_{11}H_{12}O_3$ forms a *dibromide* which melts at 122° after recrystallisation from ethyl acetate. This may be transformed into the compound $C_{11}H_{12}O_3$ by means of zinc dust and acetic acid. J. J. S.

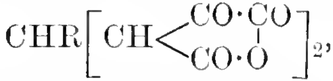
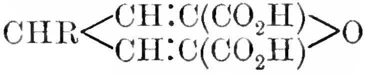
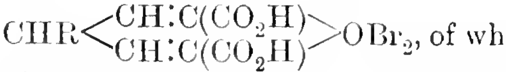
"Dande" Rubber from Rhodesia (*Bull. Imp. Inst.*, 1905, **3**, 16—18).—Two samples of "Dande" rubber, derived from a species of *Landolphia*, from the Umtali District, Rhodesia, were examined. One of the samples was rather soft and sticky, somewhat deficient in tenacity, and had the following composition: moisture, 1·2 per cent.; resin, 7·0 per cent.; caoutchouc, 88·3 per cent.; dirt and insoluble matter, 3·5 per cent.; ash, 1·7 per cent. The other sample had very good physical properties and gave the following results on analysis: moisture, 15·5 per cent.; resin, 10·7 per cent.; caoutchouc, 68·1 per cent.; dirt and insoluble matter, 5·7 per cent.; ash, 1·6 per cent.

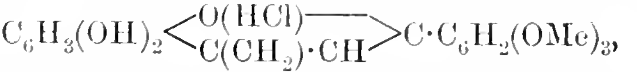
E. G.

"Muteke" Rubber from North-Eastern Rhodesia (*Bull. Imp. Inst.*, 1905, **3**, 14—16).—A specimen of "Muteke" rubber, probably derived from a new species of *Landolphia*, from North-Eastern Rhodesia, was found to have the following composition: moisture, 4·6 per cent.; resin, 12·0 per cent.; caoutchouc, 79·7 per cent.; dirt and insoluble matter, 3·7 per cent.; ash, 0·4 per cent. The product was of good elasticity and tenacity, and was completely soluble in benzene, chloroform, or carbon disulphide, and partially so in ether. E. G.

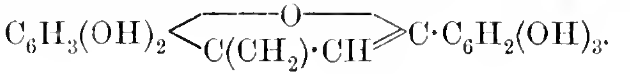
The Chemical Properties of the Copals. Bottler (*Chem. Rev. Fett. Harz. Ind.*, 1906, **13**, 51—53).—The author has examined almost all the various copals found on the market, and finds that they belong to that class of resins which consist principally of resin acids or resin-oil acids. Substances which resist the action of alkalis, resens, are also present in varying amounts. Manila copal contains 12 per cent. of resen and Zanzibar copal 6 per cent., whilst the other copals contain still less. W. P. S.

Empirical Formula and Properties of Solanin. Giovanni Romeo (*Gazzetta*, 1905, **35**, ii, 579—589. Compare Oddo and Colombano, Abstr., 1905, i, 455).—After quoting the analytical results for solanin obtained by previous investigators, the author describes a simple method for obtaining the glucoside in a pure state from the juice of the berries of *Solanum sodomæum*. The solanin prepared by the author turns brown at 280°, melts at 286°, and decomposes at a slightly higher temperature. This melting point, which is higher than that of any solanin previously extracted, is not changed by crystallising the compound from methyl alcohol (Oddo and Colombano, *loc. cit.*). Its analysis gives numbers corresponding with the formula $C_{36}H_{57}O_{13}N$ or $C_{36}H_{59}O_{13}N$. Its reactions are identical with those of solanin extracted from the potato, excepting as regards the coloration obtained with sulphuric acid of sp. gr. 1·835. T. H. P.

Researches in the Pyran Series. Edmond E. Blaise and H. Gault (*Compt. rend.*, 1906, **142**, 452—454. Compare Abstr., 1904, i, 762).—The homologues of formaldehyde condense with ethyl oxalacetate in the presence of pyridine or diethylamine to form compounds which suffer simultaneous hydrolysis and dehydration by the action of cold concentrated sulphuric acid, and yield dianhydrides of the type  $\mathrm{CHR}\left[\mathrm{CH}<\begin{matrix}\mathrm{CO\cdot CO}\\ \mathrm{CO\cdot O}\end{matrix}\right]_2$, from which the corresponding substituted diketopimelic acids are obtained by merely boiling with water. The dioximes of these acids are decomposed by boiling water to form the corresponding β-alkylglutaronitriles, whilst the acids themselves suffer dehydration by the action of sulphuric acid and yield the 4-alkylpyran-2 : 6-dicarboxylic acids,  $\mathrm{CHR}<\begin{matrix}\mathrm{CH{:}C(CO_2H)}\\ \mathrm{CH{:}C(CO_2H)}\end{matrix}>\mathrm{O}$, the dibromides,  $\mathrm{CHR}<\begin{matrix}\mathrm{CH{:}C(CO_2H)}\\ \mathrm{CH{:}C(CO_2H)}\end{matrix}>\mathrm{OBr_2}$, of which have no tendency to lose HBr and form xanthonium salts (compare Fosse, Abstr., 1903, i, 357; 1905, i, 607). M. A. W.

Synthesis of Nencki and Sieber's Gallacetein. Carl Bülow and C. Schmid (*Ber.*, 1906, **39**, 850—857. Compare Bülow and Sautermeister, Abstr., 1904, i, 262; this vol., i, 201).—7 : 8-*Dihydroxy*-2-o-m-p-*trimethoxyphenyl*-4-*methylene*-1 : 4-*benzopyran hydrochloride*,  $\mathrm{C_6H_3(OH)_2}<\begin{matrix}\mathrm{O(HCl)}\text{——}\\ \mathrm{C(CH_2)\cdot CH}\end{matrix}>\mathrm{C\cdot C_6H_2(OMe)_3}$, is readily formed when dry hydrogen chloride is passed into a solution of pyrogallol and 2 : 3 : 4-trimethoxybenzoylacetone in warm glacial acetic acid. It crystallises from alcohol containing a small amount of hydrochloric acid in red prisms melting and decomposing at 200—202°. The *sulphate*, $C_{19}H_{18}O_6,H_2SO_4$, dissolves readily in water and melts and decomposes at 124° after softening at 115°. The *picrate*, $C_{25}H_{21}O_{13}N_3$, crystallises from alcohol in red needles, melts and decomposes at 215°, and is sparingly soluble in the majority of solvents. The free base is obtained in the form of slender, violet-black needles when a hot aqueous solution of the hydrochloride is decomposed with an excess of sodium acetate solution. It melts at 183—185° and dissolves in alcohol, chloroform, carbon disulphide, or glacial acetic acid. The *diacetyl* derivative, $C_{23}H_{22}O_8$, crystallises from benzene in eosin-red needles.

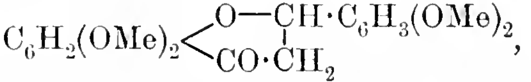
When the hydrochloride of the trimethoxy-derivative is heated with concentrated hydrochloric acid at 150—180° for a day, it is hydrolysed to the hydrochloride of Nencki and Sieber's gallacetein, the colouring matter obtained from gallacetophenone (Abstr., 1881, 811), from which gallacetein itself may be prepared by the addition of ammonia. It has the constitution



$$C_6H_3(OH)_2\Big\langle\begin{array}{c}\text{———O———}\\ C(CH_2)\cdot CH\end{array}\Big\rangle C\cdot C_6H_2(OH)_3.$$

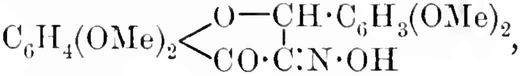
J. J. S.

Synthesis of Morin. Stanislaus von Kostanecki, Victor Lampe, and Josef Tambor (*Ber.*, 1906, **39**, 625—628. Compare Kostanecki and Tambor, Abstr., 1904, i, 426).—A very small amount of 5 : 7 : 2′ : 4′-tetramethoxyflavanone,



$$C_6H_2(OMe)_2\Big\langle\begin{array}{l}O—CH\cdot C_6H_3(OMe)_2\\ \quad\;\;\,|\\ CO\cdot CH_2\end{array},$$

is formed when 2′-hydroxy-4′ : 6′ : 2 : 4-tetramethoxychalkone is boiled with aqueous alcoholic hydrochloric acid in a reflux apparatus. It crystallises from alcohol or carbon disulphide in white needles, melts at 167—168°, dissolves in alcoholic sodium hydroxide forming a yellow solution, and gives an orange coloration with concentrated sulphuric acid. When treated with amyl nitrite and hydrochloric acid, it forms 3-iso*nitroso*-5 : 7 : 2′ : 4′-*tetramethoxyflavanone*,



$$C_6H_4(OMe)_2\Big\langle\begin{array}{l}O—CH\cdot C_6H_3(OMe)_2\\ \quad\;\;\,|\\ CO\cdot C:N\cdot OH\end{array},$$

which crystallises in light yellow needles, decomposes at 199°, dyes the cobalt mordant yellow, and dissolves in aqueous sodium hydroxide, forming a light yellow solution. When boiled with sulphuric acid in glacial acetic acid solution, the *iso*nitroso-compound yields *morin trimethyl ether*, $C_{15}H_5O_2(OH)_2(OMe)_3$, which crystallises in white needles, melts at 165°, and dissolves in aqueous sodium hydroxide to form a light yellow or in concentrated sulphuric acid to form a yellow solution having a green fluorescence, and dyes the alumina mordant light yellow.

When boiled with hydriodic acid of sp. gr. 1·9, 5 : 7 : 2′ : 4′-tetramethoxyflavanone yields 5 : 7 : 2′ : 4′-tetrahydroxyflavanol, which is identical with morin.

G. Y.

Action of Bromine on Cocaine. Anne W. K. de Jong (*Rec. trav. chim.*, 1906, **25**, 7).—When a solution of bromine in carbon tetrachloride is added to a solution of cocaine in the same solvent, a yellow oil separates, which, on shaking out with water, slowly crystallises. This *substance* melts at 85°, has the composition

$$C_{17}H_{21}O_4N,HBr,Br_2,$$

is soluble in ethyl acetate, slightly so in carbon tetrachloride, and insoluble in water and ether. It loses bromine somewhat readily, and when warmed with water evolves bromine and is converted into cocaine hydrobromide. A similar reaction is given by cinnamylcocaine.
T. A. H.

Cytisine. MARTIN FREUND and PAUL HORKHEIMER (*Ber.*, 1906, **39**, 814—825. Compare Freund and Friedmann, Abstr., 1901, i, 288; Freund, Abstr., 1904, i, 263).—The mother liquors obtained in the preparation of α-nitronitrosocytisine, melting at 244—245° (Partheil, Abstr., 1894, i, 558), contain the isomeric *β-nitronitrosocytisine*, $NO_2·C_{11}H_{12}ON_2·NO$, which melts and decomposes at 275°, and is less soluble than the α-isomeride in glacial acetic acid or alcohol. *β-Nitrocytisine hydrochloride*, $C_{11}H_{13}ON_2·NO_2,HCl$, formed by boiling the nitroso-compound with alcohol or aqueous hydrochloric acid, crystallises in long, golden-yellow needles, melts at 293°, and interacts with potassium nitrite in aqueous solution, forming β-nitronitrosocytisine. *β-Nitrocytisine*, $C_{11}H_{13}O_3N_3$, crystallises in matted, small needles or rosettes of long, slender needles and melts at 203°.

When a boiling solution of α-nitrocytisine is mixed with a hot solution of bromine in glacial acetic acid, an orange-red *perbromide* is formed; when boiled with alcohol containing sulphurous acid, this yields *bromo-α-nitrocytisine hydrobromide*, $C_{11}H_{12}ON_2Br·NO_2,HBr$, which crystallises in yellow needles containing H_2O, melts at 235°, or, when anhydrous, at 286°, and interacts with potassium nitrite in aqueous solution, forming *bromo-α-nitronitrosocytisine*,

$$NO_2·C_{11}H_{12}ON_2Br·NO,$$

melting at 245°. *Bromo-α-nitrocytisine* crystallises in slender needles and melts at 135°; the *hydrochloride*, $C_{11}H_{12}O_3N_3Br,HCl$, crystallises in microscopic, slender needles and melts above 290°; the *nitrate*, $C_{11}H_{12}O_3N_3Br,HNO_3$, melts at 238°.

The action of nitric acid on dibromocytisine leads to the formation of *dibromonitrosocytisine*, $C_{11}H_{11}O_2N_3Br_2$, which melts at 212—213°.

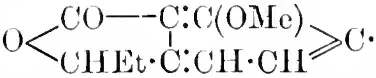
When reduced electrolytically in 50 per cent. sulphuric acid at 25—30°, with a lead beaker as cathode and a current of 5 amperes, cytisine yields *tetrahydrodeoxycytisine*, which is isolated in the form of its *hydrochloride*, $C_{11}H_{20}N_2,2HCl$; this separates as a white, crystalline powder, melts at 282°, has $[\alpha]_D - 10°15'$, and remains unchanged when heated with fuming hydrochloric acid or concentrated sulphuric acid. The *platinichloride*, $C_{11}H_{20}N_2,H_2PtCl_6$, forms hexagonal prisms and melts at 235°. The free *base* is an oil which boils at 270° under atmospheric pressure, has a strong spermic odour, is volatile with steam, blues litmus, absorbs carbon dioxide from the air, and is readily soluble in water. *Nitrosotetrahydrodeoxycytisine*, $C_{11}H_{19}N_2·NO$, formed when tetrahydrodeoxycytisine hydrochloride is boiled with concentrated nitric acid, crystallises in long needles, melts at 150°, and is readily converted into tetrahydrodeoxycytisine hydrochloride when boiled with alcoholic hydrogen chloride. The action of phenylthiocarbimide on the base leads to the formation of the *thiocarbamide*, $C_{11}H_{19}N{:}N{\cdot}CS{\cdot}NHPh$, which crystallises in needles and melts at 108°.

When heated with methyl iodide, tetrahydrodeoxycytisine yields the *hydriodide*, $C_{11}H_{19}N{:}NMe,HI$, which crystallises in plates and melts at 205—206°; the free *methyl base* is volatile with steam. The *methiodide*, $C_{11}H_{19}N{:}NMe_2I$, crystallises in long leaflets or plates, melts at 283°, and dissolves in dilute hydrochloric acid, from its solution in which it is reprecipitated on addition of ammonia. *De*-(N)-*dimethyltetrahydrodeoxycytisine*, $C_{11}H_{18}N{\cdot}NMe_2$, is formed when the methiodide is treated with silver oxide and the *ammonium hydroxide* so obtained heated with aqueous potassium hydroxide; it is a light yellow oil, boils at 266—268°, and forms *salts* which are readily soluble in water.

The *methiodide*, $NMeI{:}C_{11}H_{18}{\cdot}NMe_2$, crystallises in plates and melts at 240—241°; the *dimethiodide*, $NMeI{:}C_{11}H_{18}{\cdot}NMe_3I$, melts at 293°, and when boiled with aqueous potassium hydroxide, evolves trimethylamine and yields a viscid *oil* boiling at 255—265°.

When treated with bromine in glacial acetic acid solution, tetrahydrodeoxycytisine yields a deep yellow *perbromide*, which is converted by boiling alcohol into the *hydrobromide*, $C_{11}H_{17}BrN_2,2HBr$; this crystallises in white needles, and, when recrystallised from absolute alcohol or hydrobromic acid, melts and decomposes at 206°, but after repeated recrystallisations from water, at about 280°. G. Y.

Alkylmeconines. E. Mermod and Hugo Simonis (*Ber.*, 1906, **39**, 897—899. Compare this vol., i, 32).—When opianic acid undergoes the Grignard reaction, the yield of product is increased if constant stirring is maintained.

Ethylmeconine, 

$O<\begin{matrix}CO\text{——}C{:}C(OMe)\\ \mid \\ CHEt{\cdot}C{:}CH{\cdot}CH\end{matrix}>C{\cdot}OMe$

prepared by the action of magnesium ethyl iodide on opianic acid, separates from ethyl alcohol in monoclinic prisms and melts at 98°.

Propylmeconine, $C_{13}H_{16}O_4$, prepared by the action of magnesium propyl iodide on opianic acid, separates from ethyl alcohol in glistening needles and melts at 76°.

iso*Propylmeconine*, $C_{13}H_{16}O_4$, prepared from magnesium *iso*propyl iodide and opianic acid, separates from dilute alcohol in needles and melts at 61·5°. A. McK.

Thebaine. Martin Freund (*Ber.*, 1906, **39**, 844—850. Compare Abstr., 1905, i, 918).—*Bromocodeinone hydrobromide*,

$$C_{18}H_{18}O_3NBr,HBr,H_2O,$$

is formed when a solution of bromine in glacial acetic acid is gradually dropped into an acetic acid solution of thebaine. It is sparingly soluble in water or alcohol and crystallises from a mixture of the two in large plates melting at 197—198°. It is not rendered anhydrous when heated at 130° in a current of hydrogen, and contains one methyl group attached to nitrogen and one to carbon. The *hydrochloride* crystallises with $2H_2O$ in the form of slender needles; these turn brown at 190° and melt at 194°. When dried at 150°, one molecule of water is removed. *Bromocodeinone*, $C_{18}H_{18}O_3NBr$, crystallises from alcohol in needles which melt and decompose at 156—157°. It does not react with methyl iodide, and does not yield an acetyl derivative. When boiled with an aqueous solution of hydroxylamine hydrochloride, the hydrobromide of the base yields the *oxime* of *hydroxycodeinone*, $OH\cdot C_{18}H_{18}O_2N\colon N\cdot OH$, which melts and decomposes at 272—273° after recrystallisation from alcohol.

When reduced with sulphuric acid and iron filings, the hydrobromide yields Ach and Knorr's codeinone (Abstr., 1903, i, 849). J. J. S.

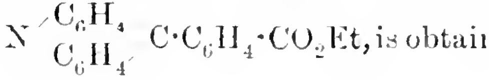
Strychnine Oxide. MAX MATTISSON (*Ber.*, 1906, **39**, 705).—Polemical. The publication of the paper on strychnine oxide by Amé Pictet and Max Mattisson (Abstr., 1905, i, 816) took place without the knowledge and consent of the latter. The author disagrees with certain statements in the paper referred to. A. McK.

Action of Sulphuryl Chloride on Indole. Chloro- and Dichloro-indoles. GIROLAMO MAZZARA and ALESSANDRO BORGO (*Gazzetta*, 1905, **35**, ii, 563—569. Compare Abstr., 1905, i, 925).—2-*Chloroindole*, prepared by the action of sulphuryl chloride (1 mol.) on indole in ethereal solution, crystallises from light petroleum in silvery scales melting and decomposing at 91·5°. It has an irritant action on the skin and a fæcal odour resembling that of scatole. It dissolves in concentrated sulphuric acid giving a green solution, and, in presence of dilute hydrochloric acid, is converted into oxindole. On heating with dilute potassium hydroxide solution, it becomes carbonised.

The action of sulphuryl chloride (2 mols.) on indole in ethereal solution yields 2 : 3-dichloroindole (compare Baeyer, Abstr., 1879, 535), which, when treated with potassium hydroxide and methyl iodide in methyl-alcoholic solution, gives 2 : 3-*dichloro*-1-*methylindole*, $C_6H_4NMeCl_2$, crystallising from dilute alcohol in slender, silky needles melting at 58°. T. H. P.

Compounds of Palladic Chloride with [Tertiary] Cyclic [Bases]. RICHARD MÖHLAU (*Ber.*, 1906, **39**, 861—863. Compare Gutbier, Abstr., 1905, i, 876; ii, 584; this vol., i, 12).—*tert*-Cyclic bases combine with palladic chloride yielding intensely coloured products, sparingly soluble in water or alcohol and insoluble in ether. Compounds of the type $PdCl_4,2C_5NH_5,HCl$ have been prepared from the following bases. Pyridine, red prisms; 2-phenylpyridine, golden-yellow plates; quinoline, bright red prisms; 2-methylquinoline, red needles; 8-phenylquinoline, orange prisms; benzothiazole, orange-red prisms and plates. Tertiary alkaloids also yield coloured compounds. J. J. S.

Ammonium Compounds. XXI. Action of Amines on Quaternary Salts of 5-Phenylacridine-*o*-carboxylic Acid. HERMAN DECKER and CARL SCHENK (*Ber.*, 1906, **39**, 748—752. Compare Abstr., 1904, i, 450).—*Ethyl* 5-*phenylacridine*-o-*carboxylate* (*acridylbenzoate*),

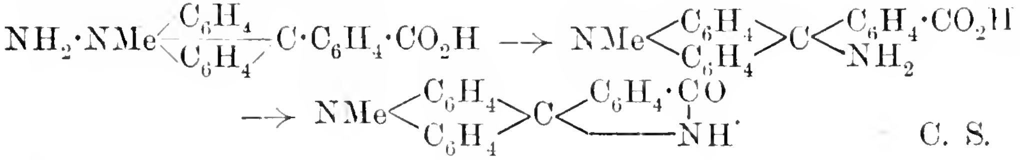


$N\begin{smallmatrix}\diagup C_6H_4\\ \diagdown C_6H_4\end{smallmatrix}C\cdot C_6H_4\cdot CO_2Et$, is obtained by passing hydrogen chloride into an alcoholic solution of the acid at 60—70°; it sublimes in bright yellow needles, melts at 161°, dissolves in dilute acids to a fluorescent solution, and is rapidly hydrolysed by boiling alkalis. The *hydriodide*, $C_{22}H_{17}O_2N,HI$, forms orange needles which melt and decompose at 216°, and separates from water and alcohol with partial decomposition; the *picrate*, $C_{22}H_{17}O_2N,C_6H_3O_7N_3$, separates from alcohol in small, yellow needles which melt at 244°; the *dichromate*, $(C_{22}H_{17}O_2N)_2,H_2Cr_2O_7,H_2O$, forms orange needles and melts when anhydrous at 141°. The *methiodide* forms garnet-red needles and melts and decomposes at 220°.

The *lactam* of 5-*amino*-5-*phenyl*-10-*methyldihydroacridine*-o-*carboxylic acid*, $NMe<\begin{smallmatrix}C_6H_4\\C_6H_4\end{smallmatrix}>C<\begin{smallmatrix}NH\\C_6H_4\end{smallmatrix}>CO$, is obtained together with the lactone by the action of ammonia on the quaternary salts of 5-phenylacridine-*o*-carboxylic acid, its esters, or the betaine compound. The lactam is more soluble in benzene than the lactone, and separates from this solvent in colourless needles which contain benzene of crystallisation, melts at 243°, and does not form fluorescent solutions in dilute acids.

The *methyl lactam*, $C_{22}H_{18}ON_2$, and the *ethyl lactam*, $C_{23}H_{20}ON_2$, are obtained in a similar way by the use of methylamine and ethylamine respectively, and are separated from the accompanying lactone by treatment with a 1—2 per cent. hydrochloric acid or by crystallisation from dilute alcohol, in which the lactams are less soluble; the methyl compound forms colourless needles and melts at 238°; the ethyl lactam also crystallises in colourless needles and melts at 203°.

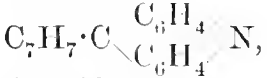
These lactams are not obtained from the lactones by the action of ammonia or amines, and it is suggested that they are derivatives of ammoniumamide, $H_4N{\cdot}NH_2$, the course of their formation being indicated by the scheme:



$$NH_2{\cdot}NMe\begin{matrix}C_6H_4\\C_6H_4\end{matrix}C{\cdot}C_6H_4{\cdot}CO_2H \longrightarrow NMe<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>C<\begin{matrix}C_6H_4{\cdot}CO_2H\\NH_2\end{matrix} \longrightarrow NMe<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>C<\begin{matrix}C_6H_4{\cdot}CO\\ \text{———}NH\end{matrix}$$

C. S.

Methyl Derivatives of 5-Phenylacridine. ALFRED SCHMID and HERMAN DECKER (*Ber.*, 1906, 39, 933—939).—5-o-*Tolylacridine*,



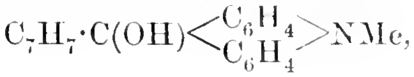
$$C_7H_7{\cdot}C\begin{matrix}C_6H_4\\C_6H_4\end{matrix}N,$$

obtained by heating *o*-toluic acid, diphenylamine, and zinc chloride for ten hours at 240—260°, melts at 212°. The *picrate*,

$$C_{20}H_{15}N{\cdot}C_6H_3O_7N_3,$$

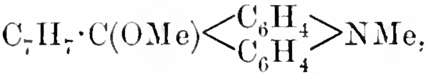
separates from alcohol in yellowish-brown prisms and melts at 226°. The *methiodide* forms dark red needles which melt and decompose at 237°. The *picrate* obtained from the carbinol base or from the quaternary salts melts at 161°.

5-*Hydroxy*-5-o-*tolyl*-10-*methyldihydroacridine*,



$$C_7H_7{\cdot}C(OH)<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>NMe,$$

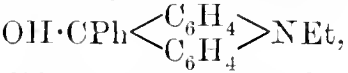
obtained from the quaternary salts by the action of alkalis, is an unstable substance and melts at 149°. By boiling methyl alcohol, it is converted into the more stable *methyl ether*,



$$C_7H_7\cdot C(OMe)<\substack{C_6H_4\\C_6H_4}>NMe,$$

which crystallises in colourless prisms and melts at 114° to a red liquid. 5-m-*Tolylacridine*, $C_{20}H_{15}N$, obtained in the same way as its isomeride, forms yellow crystals and melts at 165°. The *picrate* crystallises in small, yellow needles and melts at 253°. The *methiodide* crystallises in dark violet prisms and melts at 232°. The *picrate* obtained from the quaternary salts or from the carbinol base forms long, yellow prisms and melts at 178° and is more soluble than the tertiary picrate. The *carbinol* base is quantitatively precipitated by alkalis from solutions of the quaternary salts; it crystallises in colourless prisms, melts at 122°, and slowly turns green in the air. The *methyl ether* melts at 127—128° to a red liquid. The *ethyl ether* forms white needles and melts at 160°.

[With Th. Hock.]—5-p-*Tolylacridine*, $C_{20}H_{15}N$, forms thick, yellow prisms and melts at 189—190°. The *picrate* melts at 226°, the *methiodide* at 243°, the quaternary *picrate* at 202°, the *carbinol* base at 144°, and its *ethyl ether* at 122° to a red liquid. The last compound shows the iodoform reaction. The *ethiodide* of 5-phenylacridine is obtained in quantitative yield by heating its components at 120° for two hours. It crystallises from water in dark red leaflets and melts at about 223°, evolving ethyl iodide which can be estimated quantitatively (Abstr., 1905, i, 374). The quaternary *picrate*, obtained as well from the ethiodide as from the carbinol base, separates from alcohol in long, yellow needles and melts at 181°. The carbinol base, 5-*hydroxy*-5-*phenyl*-10-*ethyldihydroacridine*,



$$OH\cdot CPh<\substack{C_6H_4\\C_6H_4}>NEt,$$

obtained from the ethiodide by the action of alkalis, crystallises from toluene in colourless cubes and melts at 136—137°. The *ethyl ether*, $C_{23}H_{23}ON$, forms colourless needles and melts at 148° to a red liquid.

p-*Xylene*-2-*nitrile*, $C_6H_3Me_2\cdot CN$, obtained from *p*-xylidine, is a yellow oil, which boils between 223° and 226° under 730 mm. pressure and is difficultly volatile in steam.

5-m-*Xylylacridine*, $C_{21}H_{17}N$, sublimes in yellow needles and melts at 159°. The *picrate* melts at 254°.

5-p-*Xylylacridine*, $C_{21}H_{17}N$, melts at 176° and the *picrate* at 227°.

C. S.

Constitution of Thiazine and Oxazine Dyes. Friedrich Kehrmann (*Ber.*, 1906, 39, 914—926).—[With K. Modebadzé.]—3 : 9-*Dimethylphenothiazine*,  $C_6H_2Me<\substack{NH\\S}>C_6H_3Me$, obtained by rapid distillation of di-*p*-tolylamine and sulphur, crystallises in greenish-yellow leaflets, melts at 219—220°, does not combine with mineral acids or picric acid, and develops with concentrated sulphuric acid a blood-red colour due to dimethylphenthiazonium sulphate.

3 : 9-*Dimethylphenothiazonium chloride*,

$$C_6H_3Me{<}\begin{smallmatrix}N\\SCl\end{smallmatrix}{>}C_6H_3Me,$$

obtained from the preceding compound by the action of ferric chloride, forms dark green, lustrous needles; it is soluble in cold water, but the solution, slowly of itself, more rapidly in the presence of sodium acetate, deposits colourless crystals of the ψ-base. The *nitrate* forms sparingly soluble, feathery, red needles.

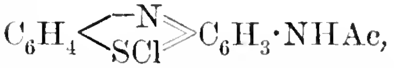
[With K. Modebadzé and V. Veselý.]—3 : 9-*Diacetylaminophenothiazine*, $C_{16}H_{15}O_2N_3S$, obtained from Lauth's violet by reduction and subsequent acetylation, forms long, colourless needles which melt at 280°, and is insoluble in water or dilute mineral acids.

3 : 9-*Diacetylaminophenothiazonium chloride*,

$$NHAc{\cdot}C_6H_3{<}\begin{smallmatrix}N\\SCl\end{smallmatrix}{>}C_6H_3{\cdot}NHAc,$$

crystallises from methyl alcohol, slightly acidified with hydrochloric acid, in long, green needles. It is not hydrolysed by cold water; the addition of sodium acetate only very slowly causes the deposition of a pale yellow ψ-base. Ammonium or sodium carbonate precipitates from the aqueous solution a dark brown, flocculent substance which disappears on boiling and in its place the crystalline ψ-base is obtained. The diacetyl compound is hydrolysed by prolonged boiling of the acidified solution. The *platinichloride*, $(C_{16}H_{13}O_2NS)_2,H_2PtCl_6$, forms violet crystals.

3-*Acetylaminophenothiazine* forms yellow needles, melts at 208°, and is insoluble in water or dilute mineral acids.

3-*Acetylaminophenothiazonium chloride*,  $C_6H_4{<}\begin{smallmatrix}N\\SCl\end{smallmatrix}{>}C_6H_3{\cdot}NHAc$, is partially hydrolysed by cold water; the addition of an alkaline carbonate produces a crystalline precipitate of the ψ-base. The *bromide*, $C_{14}H_{11}ON_2BrS$, consists of a dark brownish-violet, crystalline powder, sparingly soluble in cold water.

After discussing the properties of 3-anilinophenothiazonium chloride, 3-aminophenothiazonium chloride, Lauth's violet (3 : 9-diaminophenothiazonium chloride), and methylene-blue, the author concludes with a criticism of Hantzsch's views as to the constitution of these thionium compounds (Abstr., 1905, i, 605). C. S.

4 : 6-Dibromo-*o*-phenylenediamine. C. Loring Jackson and Frederick W. Russe (*Amer. Chem. J.*, 1906, **35**, 148—154).—4 : 6-*Dibromo*-o-*phenylenediamine*, $C_6H_2Br_2(NH_2)_2$, obtained by reducing 4 : 6-dibromo-2-nitroaniline with tin and hydrochloric acid, crystallises in plates or needles, melts at 83°, darkens on exposure to the air, and is freely soluble in alcohol and slightly so in hot water. The *hydrochloride* forms transparent needles; the *hydrobromide* crystallises in short prisms. The amine dissolves in strong sulphuric acid and, on dilution, flat, transparent prisms are deposited. The *diacetyl* derivative, $C_6H_2Br_2(NHAc)_2$, crystallises in long, white needles and melts at 227—228°.

10 : 12-*Dibromophenanthraphenazine* (5 : 7-*dibromo*-2 : 3-*diphenylenequinoxaline*), $C_{20}H_{10}N_2Br_2$, obtained by the action of phenanthra-

quinone on 4 : 6-dibromo-*o*-phenylenediamine, crystallises in slender, yellow needles, melts at 248°, is soluble in hot benzene or chloroform, slightly so in alcohol, ether, or acetone, and is insoluble in light petroleum or water.

5 : 7-*Dibromo*-2 : 3-*diphenylquinoxaline*, $C_{20}H_{12}N_2Br_2$, obtained by the condensation of the amine with benzil, crystallises from dilute alcohol in long, white needles, melts at 149—150°, and is soluble in the usual organic solvents and insoluble in water.

By the action of tetrabromo-*o*-benzoquinone on the amine, a red, tarry mass was obtained from which no definite compound could be isolated. E. G.

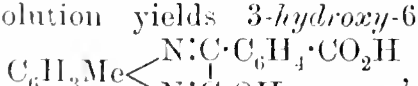
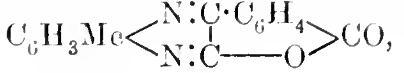
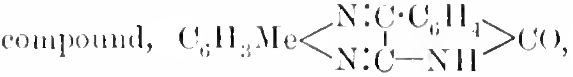
[Basic Dyes from Formyl-*m*-diamines.] ANILINFARBEN- & EXTRACT-FABRIKEN VORM. JOH. R. GEIGY (D.R.-P. 161699. Compare Abstr., 1904, i, 530).—The formyl derivatives of *m*-diamines (Abstr., 1903, i, 522) condense with alkylated *m*-diamines or alkylated *m*-aminophenols when heated at 150—250° with ammonium salts or salts of amines. Orange dyes, suitable for use with a tannin mordant or on leather, are thus obtained. C. H. D.

[3 : 5-Dichloro-4′-dimethylamino-4-hydroxydiphenylamine.] FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 161665).—The indophenol prepared from 2 : 6-dichlorophenol and *as*-dimethyl-*p*-phenylenediamine yields on reduction with sodium sulphide 3 : 5-*dichloro*-4′-*dimethylamino*-4-*hydroxydiphenylamine*,

$$OH\cdot C_6H_2Cl_2\cdot NH\cdot C_6H_4\cdot NMe_2,$$

which forms small, white crystals and readily oxidises in air to the indophenol. The preparation may also be carried out without isolating the dichlorophenol by adding 2 mols. of sodium hypochlorite to 1 mol. of sodium phenoxide, adding the calculated quantity of *as*-dimethyl-*p*-phenylenediamine, oxidising, and reducing the indophenol. Blue dyes are obtained on fusing the product with sulphur and sodium sulphide. C. H. D.

Condensation of *o*-Diamines with Phthalonic Acid. CAMILLO MANUELLI and CONCETTO MASELLI (*Gazzetta*, 1905, **35**, ii, 572—579. Compare Manuelli and Silvestri, Abstr., 1904, i, 784).—When heated together in alcoholic solution, ethylenediamine and phthalonic acids yield the *compound*  $CH_2{<}\begin{array}{l}CH_2{-}{-}N\\ N{:}C(OH)\end{array}{>}C\cdot C_6H_4\cdot CO_2H$, which melts and decomposes at 176°, and, in aqueous solution, decomposes barium and calcium carbonates. The *silver* salt, $C_{11}H_8O_3N_2Ag_2$, was prepared and analysed.

The condensation of 1-tolylene-3 : 4-diamine and phthalonic acid in aqueous or alcoholic solution yields 3-*hydroxy*-6(or 7)-*methylquinoxaline*-2-*benzoic acid*,  $C_6H_3Me{<}\begin{array}{l}N{:}C\cdot C_6H_4\cdot CO_2H\\ N{:}C\cdot OH\end{array}$, which separates as a white, crystalline powder melting and decomposing at 245°. The *calcium* salt, $(C_{16}H_{11}O_3N_2)_2Ca,8H_2O$, crystallises in silky needles. The *lactone*,  $C_6H_3Me{<}\begin{array}{l}N{:}C\cdot C_6H_4\\ N{:}C{-}{-}O\end{array}{>}CO$, prepared by heating the acid at a temperature slightly above its melting point, crystallises from benzene in elongated prisms or from alcohol in iridescent scales melting at 225°. On treatment with alcoholic ammonia solution, the lactone is converted into the *imino*-compound,  $C_6H_3Me<\begin{array}{l}N{:}C\cdot C_6H_4\\ \quad | \\ N{:}C—NH\end{array}>CO$, which separates from alcohol in slender, pale yellow needles melting at 303°; the *aurichloride*, $C_{16}H_{11}ON_3,HAuCl_4$, forms pale yellow prisms, and the *platinichloride*, $(C_{16}H_{11}ON_3)_2,H_2PtCl_6$, intensely yellow, acicular crystals.

On heating molecular proportions of *m*-nitro-*p*-toluidine and phthalonic acid in alcoholic solution in a sealed tube, condensation takes place with formation of a *compound*,

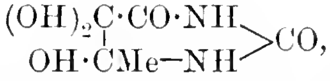
$$CMe\begin{array}{l}<\\ \leqslant\end{array}\begin{array}{l}CH{:}C(NO_2)\\ CH——CH\end{array}\begin{array}{l}>\\ \geqslant\end{array}C\cdot N{:}CH\cdot C_6H_4\cdot CO_2H\ (?),$$

which crystallises from benzene in iridescent, yellow needles melting at 198° and dissolves in solutions of the alkali hydroxides or carbonates. T. H. P.

Piperazine Benzoate and Salicylate. A. Astruc (*Bull. Soc. chim.*, 1906, [iii], **35**, 169—171. Compare Abstr., 1905, i, 382, 671). —*Piperazine benzoate*, $C_4H_{10}N_2(C_7H_6O_2)_2$, is precipitated when solutions of the acid and of the base in alcohol are mixed. It crystallises in small lamellæ, sublimes at 120°, has a faint odour of benzoic acid, dissolves in 4·2 parts of water, in 16·3 parts of alcohol (90 per cent.), and in 46·4 parts of absolute alcohol at 15°, is alkaline to helianthin, and acid to phenolphthalein. In presence of the latter indicator, 1 mol. of potassium hydroxide is required to produce neutrality.

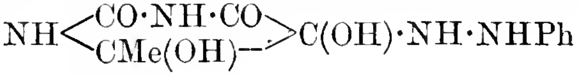
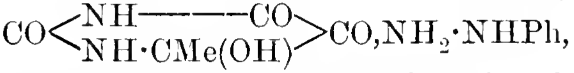
Piperazine salicylate, prepared in the same manner as the benzoate, forms colourless needles, is inodorous, has a sweet taste, and sublimes at 160°. It dissolves in 90 parts of water, in 200 parts of alcohol (90 per cent.), and in 450 parts of absolute alcohol at 15°, is neutral to helianthin, and acid to phenolphthalein. In presence of the latter indicator, 1 mol. of potassium hydroxide is required to produce neutrality. The reactions of the solutions of these salts with solutions of a number of metallic salts are given in the original. T. A. H.

Trihydroxymethyldihydrouracil. Robert Behrend and Hans Osten [with Carl Beer] (*Annalen*, 1905, **343**, 133—151).—In order to account for the peculiarities observed in the oxidation of the various methyl- and dimethyl-uracils (Behrend and Grünewald, Abstr., 1902, i, 834), it was thought that trihydroxymethyl- or dimethyl-dihydrouracil was formed as an intermediate product. These substances have now been more minutely investigated.

a-Trihydroxymethyldihydrouracil,  $\begin{array}{l}(OH)_2C\cdot CO\cdot NH\\ \quad\ \ |\\ OH\cdot CMe—NH\end{array}>CO$, has been prepared from methyluracil; the latter is first nitrated by treatment with a mixture of nitric acid and phosphoric oxide, the nitrouracil crystallising in prisms or leaflets melting and decomposing at 290°. Aminomethyluracil is obtained by reduction of the nitro-derivative in ammoniacal solution with amalgamated aluminium. When treated with bromine in suspension in water, the trihydroxy-compound is formed as white crystals melting at 127—128°; the melting point depends on the rate of heating, a temperature of 136° being occasionally observed. When heated at 110°, it loses $2H_2O$ and is converted into an insoluble powder which decomposes at 140—145° and gives a blue coloration with ferric chloride.

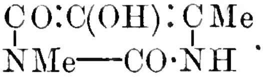
β-Trihydroxymethyldihydrouracil is prepared by dissolving dibromohydroxymethyluracil in potassium hydroxide, neutralising with hydrochloric acid, and then evaporating over sulphuric acid; it forms crystals melting at 116—117°; it is converted into the α-derivative by treatment with acids, and is formed from the α-isomeride by heating in neutral solution or by very cautious treatment with alkali hydroxides.

With ethyl alcohol, the α-compound yields an *α-hydroxydiethoxymethyldihydrouracil*,  $\left.\begin{array}{l}(OEt)_2C\cdot CO\cdot NH\\ OH\ \ CMe{-}{-}NH\end{array}\right>CO$, which forms crystals melting at 180—182°, and is reconverted into the trihydroxy-derivative by water at a low temperature. The β-trihydroxy-derivative also yields a *β-hydroxydiethoxymethyldihydrouracil*, which sinters at 105° and melts at 134—136°, and is reconverted into the trihydroxy-compound by water.

The two isomerides also give with phenylhydrazine two distinct compounds; with phenylhydrazine acetate in aqueous solution, the α-derivative yields a *compound*,  $NH\left<\begin{array}{l}CO\cdot NH\cdot CO\\ CMe(OH){-}{-}\end{array}\right>C(OH)\cdot NH\cdot NHPh$ or  $CO\left<\begin{array}{l}NH{-}{-}{-}{-}{-}{-}CO\\ NH\cdot CMe(OH)\end{array}\right>CO,NH_2\cdot NHPh$, which forms yellow crystals decomposing at 170—180° and behaves as a hydrazide, phenylhydrazine being set free by alkali hydroxides. The β-derivative melts at 125° and has similar properties.

When oxidised by permanganate in the presence of potassium hydrogen carbonate, both the uracils yield potassium acetoxalurate, but, in the presence of excess of alkali hydroxide, an oxalate and acetylcarbamide. When the oxidation is carried out by permanganate at a higher temperature, oxaluric acid is formed. The acetallanturic acid, formed by boiling β-trihydroxymethyldihydrouracil with water, is oxidised by chromic acid to parabanic acid.

So far, the isomerism of the trihydroxymethyldihydrouracils has not been accounted for. K. J. P. O.

Oxidation of Methylated Methyluracils. ROBERT BEHREND and CARL HUFSCHMIDT (*Annalen*, 1905, **343**, 155—168).—It was observed (Abstr., 1903, i, 739) that trimethyluracil yielded on oxidation hydroxy-β-dimethyluracil,  $\begin{array}{l}CO{:}C(OH){:}CMe\\ NMe{-}{-}CO\cdot NH\end{array}$. Since it was possible that this substance was formed from a small quantity of β-dimethyluracil present as an impurity in the trimethyluracil, the experiments have been repeated.

Pure trimethyluracil was prepared by methylating α-dimethyluracil with methyl iodide and potassium hydroxide; it melted at 111—112°, and was oxidised by a 2 per cent. solution of permanganate in the presence of acetic acid. The hydroxy-β-dimethyluracil thus obtained crystallised in rhombic leaflets decomposing at 335°. On further oxidation, it yielded *s*-acetylmethylcarbamide.

Dimethyluracil yields on oxidation hydroxymethyluracil, and probably also hydroxy-α-dimethyluracil, which is obtained in slender needles melting at 254—258°.

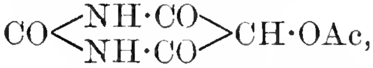
β-Dimethyluracil gives on oxidation the hydroxy-β-dimethyluracil previously described; it is coloured deep blue by ferric chloride. Its acetyl derivative was prepared, and was identical with the substance obtained from trimethyluracil. K. J. P. O.

Nitration of Trimethyluracil. ROBERT BEHREND and CARL HUFSCHMIDT (*Annalen*, 1905, **343**, 168—175).—Trimethyluracil was nitrated with a mixture of sulphuric acid and nitric acid saturated with oxides of nitrogen. When the nitration is carried out at as low a temperature as possible, a green *substance*, $C_7H_6O_4N_4$ or $C_7H_8O_4N_4$, an intermediate product, was obtained; it melted and decomposed at 168°. When reduced with tin and hydrochloric acid at 0°, a sparingly soluble *compound*, $C_7H_8O_3N_4$, $C_{14}H_{18}O_6N_8$, or $C_7H_{10}O_3N_4$, is formed, which melts and decomposes at 227° and is soluble in, but decomposed by, potassium hydroxide; it can be recrystallised from concentrated hydrochloric or sulphuric acid or acetic acid, from which it separates in dark yellow needles.

When the reduction is carried out at the ordinary temperature, a readily soluble *compound*, $C_7H_9O_4N_3$, is produced; it crystallises in long needles melting at 215°; it is readily soluble in water, acids, and alkali hydroxides, and gives with ferric chloride an intense blue coloration. Its *acetyl* derivative melts at 162—172°.

When the trimethyluracil is nitrated at the ordinary temperature, *nitrodimethyluracilcarboxylic acid*, $C_7H_7O_6N_3,2H_2O$, which melts and decomposes at 139—140°, and nitrodimethyluracil (m. p. 150—154°) are formed. The acid is obtained in larger proportion when the mixture is cooled. K. J. P. O.

Dialuric Acid. ROBERT BEHREND and HERMANN FRIEDRICH (*Annalen*, 1906, **344**, 1—18. Compare Menschutkin, this Journal, 1876, i, 907).—On preparing potassium, sodium, and ammonium dialurates by Menschutkin's methods (*loc. cit.*), the author obtained salts only of the type $C_4H_3O_4N_2M'$. This is in agreement with Koech's results (Abstr., 1901, i, 262), and Menschutkin's supposed salts of the type $C_7H_8O_{10}N_4M_2'$, are considered to be non-existent.

When finely powdered and boiled with acetic anhydride, dialuric acid forms the *acetyl* derivative,  $CO<\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}>CH\cdot OAc$, which crystallises in white prisms or leaflets, melts at 210—212°, is readily soluble in water or alcohol, but less so in ether, and when recrystallised from boiling water decomposes partially, yielding a product melting and becoming red at 200—210°. It forms a violet *precipitate* with barium hydroxide in aqueous solution, and interacts with potassium acetate in 95 per cent. alcohol, forming a *potassium* salt,

$$C_6H_7O_6N_2K,H_2O;$$

this is obtained as a fine crystalline precipitate, loses H_2O over soda-lime in a vacuum, melts and decomposes at 300—303°, has an acid reaction in aqueous solution, is not precipitated from its aqueous solution by barium or calcium chloride, but with lead acetate forms a *precipitate* consisting of white leaflets, and reduces cold silver nitrate or ammoniacal silver solutions. Acetyldialuric acid interacts with alloxan in aqueous solution at 40°, forming *acetylalloxantin*,

$$C_{10}H_8O_9N_4,H_2O,$$

which crystallises in thin leaflets resembling those of alloxantin, loses H_2O over sulphuric acid in a vacuum, melts and decomposes with ebullition at 263—265°, and is hydrolysed slowly by hot water with formation of alloxantin.

Benzoyldialuric acid, $C_{11}H_8O_5N_2$, formed by heating dialuric acid with benzoyl chloride at 190—200°, crystallises from alcohol in prisms or leaflets, melts at 209—210°, is readily soluble in alcohol, but less so in ether, and only sparingly so in cold water or benzene, and with barium hydroxide in aqueous solution gives, after some time, a bluish-violet coloration. It interacts with alloxan in hot aqueous solution, forming *benzoylalloxantin*, $C_{15}H_{10}O_9N_4,H_2O$ or $1\frac{1}{2}H_2O$, which crystallises from hot water in colourless, hexagonal leaflets, melts at 253—255°, and with barium hydroxide in aqueous solution yields a white precipitate changing to bluish-violet.

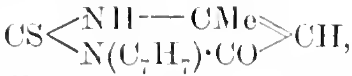
If acetylalloxantin is dissolved in pyridine, acetic anhydride added, and the mixture evaporated over sulphuric acid and lime in a vacuum, there is obtained a crystalline *additive* product, $C_{10}H_8O_9N_4,C_5H_5N$, which dissolves in dilute sodium hydroxide, yielding an odour of pyridine. The action of ammonium carbonate on acetylalloxantin in aqueous solution leads to the formation of murexide (compare Piloty and Finckh, Abstr., 1904, i, 820); contrary to the statement of these authors, murexide crystallises with less than $1H_2O$, or loses part of its water of crystallisation when dried in air; at 120°, it commences to decompose with evolution of ammonia.

Quinol diacetate resembles the dialkyl ethers of quinol in that it does not interact with quinone in cold alcohol or ethereal solution; this is of importance in view of the formation of alloxantin from acetyldialuric acid and the parallel drawn by Piloty and Finckh (*loc. cit.*) between the formation of alloxantin and that of quinhydrone.

*iso*Dialuric acid, which contains the grouping $-CH(OH)\cdot C(OH)_2-$, does not form a compound resembling alloxantin with alloxan or with dialuric acid. As *iso*dialuric acid is easily soluble in water, contains 1 mol. of water of constitution, and interacts readily with hydroxylamine hydrochloride forming an oxime, it has most probably the molecular formula $C_4H_6O_4N_2$, and is not itself a compound of the nature of alloxantin (compare Behrend and Roosen, Abstr., 1888, 581).

G. Y.

Action of Thiocarbimides on Ethyl Aminocrotonate. ROBERT BEHREND and HANS HENNICKE (*Annalen*, 1906, **344**, 19—29. Compare Behrend, Meyer, and Buchholtz, Abstr., 1901, i, 136; Behrend and Hesse, Abstr., 1904, i, 379).—*Ethyl iminoacetyl*-p-*tolylthiomalonamate*, $NH:CMe\cdot CH(CO_2Et)\cdot CS\cdot NH\cdot C_7H_7$, or *ethyl aminoethylidene*-p-*tolylthiomalonamate*, $NH_2\cdot CMe:C(CO_2Et)\cdot CS\cdot NH\cdot C_7H_7$, is formed by the interaction of *p*-tolylthiocarbimide with ethyl aminocrotonate during some weeks at the laboratory temperature, or, together with small amounts of thion-*p*-tolylmethyluracil, more quickly on the water-bath; it crystallises from alcohol in yellow, prismatic needles, melts at 125—130°, and is moderately soluble in alcohol or benzene, but is almost insoluble in water or ether.

Thion-p-tolylmethyluracil,  $CS\left<\begin{matrix}NH{-}{-}CMe\\ N(C_7H_7)\cdot CO\end{matrix}\right>CH$, crystallises in slender, almost colourless needles, melts at 278—279°, and is soluble in dilute sodium hydroxide.

The action of allylthiocarbimide on ethyl aminocrotonate for five weeks at the laboratory temperature, or for four to five hours at 70°, leads to the formation of *ethyl iminoacetylallylthiomalonamate*, $C_{10}H_{16}O_2N_2S$, which crystallises from 95 per cent. alcohol in snow-white, slender needles and melts at 105—106°. No thionmethylallyluracil is formed.

Ethyl iminoacetylethylthiomalonamate, $C_9H_{16}O_2N_2S$, but no thionmethylethyluracil, is formed by the interaction of ethylthiocarbimide and ethyl aminocrotonate for two months at the laboratory temperature; the ester crystallises from alcohol in snow-white needles and melts at 130—131°. When digested with silver carbonate and alcohol, the ester is converted into *ethyl iminoacetylethylmalonamate*,

$$NH\colon CMe\cdot CH(CO_2Et)\cdot CO\cdot NHEt,$$

which separates from light petroleum in matted, slender needles or, on exposure to air, in transparent, compact crystals containing H_2O.

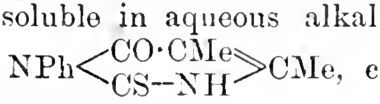
Benzylthiocarbimide, boiling at 140—141° under 17 mm. pressure, is obtained in a yield of 23 per cent. of the theoretical by distilling benzyl thiocyanate four times under the atmospheric pressure and fractionating the product in a vacuum. With ethyl aminocrotonate, it forms *ethyl iminoacetylbenzylthiomalonamate*, $C_{14}H_{18}O_2N_2S$, slowly at the laboratory temperature, more quickly at 70°; the ester separates from alcohol in large, greenish-yellow crystals and melts at 115—116°.

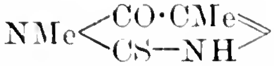
The action of phenylthiocarbimide on methyl aminocrotonate leads to the formation, slowly at the laboratory temperature, more quickly on the water-bath, of methyl iminoacetylphenylthiomalonamate, or at 130—140° to the formation of thionphenylmethyluracil, melting at 253—254°. The *ester*, $NH\colon CMe\cdot CH(CO_2Me)\cdot CS\cdot NHPh$, separates from alcohol in light yellow crystals, melts at 153—154°, and is slightly soluble in dilute sodium hydroxide.

Ethyl methyliminoacetylphenylthiomalonamate,

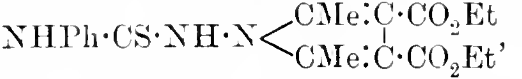
$$NMe\colon CMe\cdot CH(CO_2Et)\cdot CS\cdot NHPh,$$

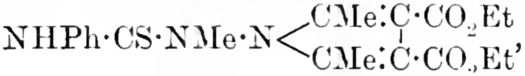
formed by the action of phenylthiocarbimide on ethyl methylaminocrotonate, separates from alcohol in transparent, dark yellow crystals and melts at 107—108°.

The action of phenylthiocarbimide on ethyl β-amino-α-methylcrotonate leads to the formation of thionphenyldimethyluracil and a *product* which separates from alcohol in colourless crystals, melts at 154—155°, and is soluble in aqueous alkali hydroxides. *Thionphenyldimethyluracil*,  $NPh\left<\begin{matrix}CO\cdot CMe\\ CS{-}{-}NH\end{matrix}\right>CMe$, crystallises in slender needles and melts at 254—255°.

Thiontrimethyluracil,  $NMe<\genfrac{}{}{0pt}{}{CO\cdot CMe}{CS-NH}>CMe$, formed from methylthiocarbimide and ethyl β-amino-α-methylcrotonate at 70—80°, crystallises in snow-white, slender needles and melts at 255—256°. G. Y.

Hydroxyphenylrosindulines. KALLE & Co. (D.R.-P. 160789 and 160815. Compare Abstr., 1905, i, 554, 840).—*p*-Aminophenol condenses with either benzeneazomonoaryl-α-naphthylamines or monoaryl-1 : 4-diaminonaphthalenes on fusion or on boiling in a reflux apparatus with alcohol or water. The products obtained are bluer in colour than those derived from non-arylated compounds, and probably contain only two hydroxyl groups. C. H. D.

Ethyl 1-Phenylthiouramino-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate. CARL BÜLOW and CONSTANTIN SAUTERMEISTER (*Ber.*, 1906, **39**, 647—651. Compare Abstr., 1904, i, 690; Bülow and Krafft, Abstr., 1903, i, 196; Bülow, Riess, and Sautermeister, Abstr., 1905, i, 660).—*Ethyl* 1-*phenylthiocarbamido*-2 : 5-*dimethylpyrrole*-3 : 4-*dicarboxylate*,  $NHPh\cdot CS\cdot NH\cdot N<\genfrac{}{}{0pt}{}{CMe{:}C\cdot CO_2Et}{CMe{:}C\cdot CO_2Et}$, is formed by boiling (1) ethyl 1-amino-2 : 5-dimethylpyrrole 3 : 4-dicarboxylate with phenylthiocarbimide or (2) 4-phenylthiosemicarbazide with ethyl diacetylsuccinate in alcoholic solution in a reflux apparatus. It crystallises in glistening, white, rhombic needles, melts at 197°, is readily soluble in alcohol, ether, benzene, pyridine, aqueous ammonia, or dilute alkali hydroxide, and is precipitated from its alkaline solutions on acidification with acetic acid. When treated with methyl sulphate in ice-cooled, aqueous potassium hydroxide solution, it forms *ethyl* 1-β-*phenylmethylthiocarbamido*-2 : 5-*dimethylpyrrole*-3 : 4-*dicarboxylate*,



$$NHPh\cdot CS\cdot NMe\cdot N<\genfrac{}{}{0pt}{}{CMe{:}C\cdot CO_2Et}{CMe{:}C\cdot CO_2Et}$$

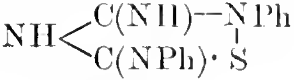
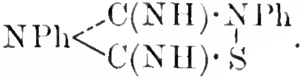
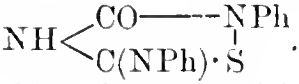
which crystallises from alcohol in needles and melts at 154°, together with a small quantity of a *substance* which is precipitated from the mother liquors by carbon dioxide or acetic acid, and melts at 80—90°, or, after three recrystallisations from alcohol, at 214—215°.

When shaken with benzoyl chloride and aqueous potassium hydroxide, ethyl 1-phenylthiocarbamidodimethylpyrroledicarboxylate yields ethyl 1-benzoylamino-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate, melting at 124°.

Hydrazodicarbonanilide, formed by the action of phenylcarbimide on 4-phenylthiosemicarbazide in warm alcoholic solution, crystallises in delicate, glistening, white leaflets and melts at 212—213°. Curtius and Burkhardt, who prepared this substance by the action of iodine or of heat on phenylsemicarbazide, found it to crystallise in prisms and melt at 245° (Abstr., 1899, i, 137). G. Y.

Reduction in the Diphenylmethane Series. HENRI DUVAL (*Compt. rend.*, 1906, **142**, 341—342. Compare Abstr., 1905, i, 651). —2 : 2′ : 4 : 4′-*Tetraminodiphenylmethane*, obtained when 4 : 4′-diamino-2 : 2′-azodiphenylmethane is reduced with stannous chloride in hydrochloric acid solution, forms colourless crystals, soluble in alcohol or water, insoluble in ether, and yields a *dibenzoyl* derivative melting at 275°, which is sparingly soluble in alcohol and insoluble in water. When 4 : 4′-diamino-2 : 2′-azodiphenylmethane is reduced by zinc dust in alkaline solution, 4 : 4′-diaminoacridine is produced; this forms yellow needles melting at 284° (Schöpff gives 281°, Abstr., 1894, i, 598). M. A. W.

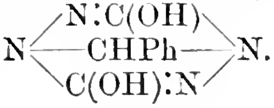
Oxidation Products of Thiocarbamides and their Isomerides.

K. Dost (*Ber.*, 1906, **39**, 863–866. Compare Hector, Abstr., 1889, 872).—When the product, obtained by the oxidation of phenylthiocarbamide with hydrogen peroxide, is boiled gently with fuming hydrochloric acid for 3·5 hours, it is converted into a *compound*, $C_{14}H_{11}ON_3S$, which crystallises from alcohol in long, glistening needles melting at 162°. The compound does not form salts and is not acetylated when boiled with acetic anhydride. It has not been found possible to replace a second NH group in the oxidation product by oxygen, and the formula  $NH<\begin{matrix}C(NH)-NPh\\ \quad\quad\quad\quad | \\C(NPh)\cdot S\end{matrix}$ is suggested instead of Hector's formula  $NPh<\begin{matrix}C(NH)\cdot NPh\\ \quad\quad\quad\quad | \\C(NH)\cdot S\end{matrix}$. The oxygen compound is then  $NH<\begin{matrix}CO-NPh\\ \quad\quad\quad\quad | \\C(NPh)\cdot S\end{matrix}$. The oxidation product of *p*-tolylthiocarbamide, when treated in a similar manner, yields a *product*, $C_{16}H_{15}ON_3S$, melting at 163°.

The two oxidation products are readily transformed into isomerides when heated with alcoholic ammonia at 145—150° for 2·25 hours. The derivative from the oxidation product of phenylcarbamide melts at 198° and the homologue at 203°. Both compounds have lost their basic properties. The phenyl derivative yields an *acetyl* compound, $C_{14}H_{11}N_4SAc$, which melts at 235°. The *p*-tolyl derivative combines with phenylcarbimide, yielding a *compound* $C_{14}H_{12}N_4S,2CONPh$, melting at 168°. J. J. S.

Condensation of Aldehydes with *s*-Dihydrotetrazines.

Robert Stollé (*Ber.*, 1906, **39**, 826—827. Compare Abstr., 1903, i, 721; 1905, i, 249; also Ruhemann and Merriman, Trans., 1905, **87**, 1768).—It has been shown previously that diphenyl-*s*-dihydrotetrazine condenses with benzaldehyde and, since a molecular rearrangement, as suggested by Ruhemann and Merriman, is impossible in this case, the original constitutional formulæ are regarded as established.

The benzylidene derivative of dicarbamide described by Curtius and Heidenreich (Abstr., 1895, i, 12) is regarded as having the constitutional formula  $N\begin{matrix}N{:}C(OH)\\ CHPh\\ C(OH){:}N\end{matrix}N$. J. J. S.

Influence of Methyl Groups on the Shade of Dyes containing Two Triphenylmethane Groups joined by a Glutaconic Aldehyde Group. FRITZ REIZENSTEIN and JULIUS ROTHSCHILD (*J. pr. Chem.*, 1906, [ii], 73, 192—206. Compare Reizenstein and Runge, Abstr., 1905, i, 300; Zincke, Heuser, and Möller, Abstr., 1904, i, 921).—The action of dinitrophenylpyridinium chloride on aminotetramethyldiaminotriphenylmethanes in alcoholic solution on the water-bath leads to the formation of products of the type

$$\begin{array}{l}C_6H_4\cdot N{:}CH\cdot CH{:}CH\cdot CH{:}CH\cdot NH_2Cl\cdot C_6H_4\cdot CH(C_6H_4\cdot NMe_2)_2.\\ CH(C_6H_4\cdot NMe_2)_2\end{array}$$

When oxidised with lead peroxide in acetic acid, these substances form solutions which dye purer and more intense shades than the corresponding triphenylmethane dyes; as compared with each other, those containing methyl groups in the ortho-position give weaker colours.

The *hydrochloride* $C_{53}H_{61}N_6Cl$, formed from 4-amino-4′ : 4″-tetramethyldiamino-3-methyltriphenylmethane, is obtained as a red powder melting at about 95°; the *dye* colours cotton-wool, mordanted with tannin, dark blue.

The *hydrochloride* $C_{53}H_{61}N_6Cl$, obtained from 4-amino-4′ : 4″-tetramethyldiamino-2-methyltriphenylmethane, is yellowish-green and melts at about 95°; the *dye* colours cotton-wool, mordanted with tannin, dark corn-flower blue.

The *hydrochloride* $C_{53}H_{61}N_6Cl$, formed from 2-amino-4′ : 4″-tetramethyldiamino-5-methyltriphenylmethane, is yellowish-brown, sinters at 75°, and melts at about 95°. The corresponding *ammonium hydroxide*, $C_{53}H_{61}N_6\cdot OH$, is a reddish-brown powder melting at about 81°. The *dye* colours cotton-wool, mordanted with tannin and potassium hydrogen tartrate, indigo-blue.

The *hydrochloride* $C_{53}H_{61}N_6Cl$, formed from 3-amino-4′ : 4″-tetramethyldiamino-4-methyltriphenylmethane, is greenish-yellow and melts at 78°. The *dye* colours mordanted cotton-wool intense green.

The *hydrochloride* $C_{53}H_{61}N_6Cl$, formed from 3-amino-4′ : 4″-tetramethyldiamino-5-methyltriphenylmethane, is dark red, sinters at 102°, and melts at 115°. The *dye* colours cotton-wool, mordanted with tannin, dark greenish-blue.

The *hydrochloride* $C_{53}H_{61}N_6Cl$, formed from 3-amino-4′ : 4″-tetramethyldiamino-6-methyltriphenylmethane, is obtained as a red powder melting at about 130°. The *dye* colours cotton-wool, mordanted with tannin, bluish-green.

The *hydrochloride* $C_{57}H_{69}N_6Cl$, formed from 4-amino-4′ : 4″-tetramethyldiamino-2′ : 2″ : 3-trimethyltriphenylmethane, is brownish-yellow, sinters at 90°, and melts at 115°. The *dye* is a weak bluish-green.

The *hydrochloride* $C_{57}H_{69}N_6Cl$, formed from 4-amino-4′ : 4″-tetramethyldiamino-2 : 2′ : 2″-trimethyltriphenylmethane, is yellowish-brown, sinters at 90°, and melts at 109°. The *dye* colours cotton-wool, mordanted with tannin, a weak green.

The *hydrochloride* $C_{57}H_{69}N_6Cl$, formed from 2-amino-4′ : 4″-tetramethyldiamino-2′ : 2″ : 5-trimethyltriphenylmethane, is a dark brown powder which sinters at 90° and melts at 112°. The *dye* colours cotton-wool, mordanted with tannin, a weak green.

The preceding three derivatives of trimethyltriphenylmethane dissolve in glacial acetic acid forming intensely green solutions. No diminution in the intensity consequent on the introduction of methyl groups the *o*-position can be observed. This applies also to the following three condensation products.

The *hydrochloride* $C_{57}H_{69}N_6Cl$, formed from 3-amino-4′ : 4″-tetramethyldiamino-2′ : 2″ : 4-trimethyltriphenylmethane, is dark yellow, sinters at 85°, and melts at 115°. The *dye* colours cotton-wool, mordanted with tannin, a weak light green.

The yellowish-brown *hydrochloride*, $C_{57}H_{69}N_6Cl$, formed from 3-amino-4′ : 4″-tetramethyldiamino-2′ : 2″ : 5-trimethyltriphenylmethane, sinters at 85° and melts at 113°. The *dye* colours cotton-wool, mordanted with tannin, a weak light green.

The brown *hydrochloride*, $C_{57}H_{69}N_6Cl$, formed from 3-amino-4′ : 4″-tetramethyldiamino-2′ : 2″ : 6-trimethyltriphenylmethane, sinters at 105° and melts at 115°. The *dye* colours cotton-wool, mordanted with tannin, a weak light green.

The red *hydrochloride*, $C_{51}H_{57}N_6Cl$, formed from *o*-aminoleucomalachite-green, sinters at 40° and melts at 68°. The *dye* colours cotton-wool, mordanted with tannin, bluish-green.

The green *hydrochloride*, $C_{51}H_{57}N_6Cl$, formed from *m*-aminoleucomalachite-green, melts at 78°. The *dye* colours cotton-wool, mordanted with tannin, intense emerald-green.

The green *hydrochloride*, $C_{51}H_{57}N_6Cl$, formed from *p*-aminoleucomalachite-green, melts at about 72°. The *dye* colours cotton-wool, mordanted with tannin, dark blue.

The dark yellowish-brown *hydrochloride*, $C_{55}H_{65}N_6Cl$, formed from 2-amino-4′ : 4′-tetramethyldiamino-2′ : 2″-dimethyltriphenylmethane, melts at 102°. The *dye* colours cotton-wool, mordanted with tannin, a weak bluish-green.

The yellowish-brown *hydrochloride*, $C_{55}H_{65}N_6Cl$, formed from 3-amino-4′ : 4″-tetramethyldiamino-2′ : 2″-dimethyltriphenylmethane, melts at about 82°. The *dye* colours cotton-wool, mordanted with tannin, yellowish-green.

The yellow *hydrochloride*, $C_{55}H_{65}N_6Cl$, formed from 4-amino-4′ : 4″-tetramethyldiamino-2′ : 2″-dimethyltriphenylmethane, sinters at 60° and melts at 78°. The *dye* colours cotton-wool, mordanted with tannin and potassium hydrogen tartrate, lilac.

2-Chloro- and 4-chloro-pyridine dissolve in 1-chloro-2 : 4-dinitrobenzene, forming a yellow solution which becomes dirty brown when heated at 190—200° and a red solution which solidifies to a yellowish-red mass respectively. In neither case does any interaction take place, as the constituents of the mixtures can be separated by treatment of the products with ether. G. Y.

Liquid-crystalline Substances. [Azoxy-compounds.] DANIEL VORLÄNDER (*Ber.*, 1906, **39**, 803—810. Compare Vorländer and Meyer, Abstr., 1902, i, 328; Meyer and Dahlem, Abstr., 1903, i, 448).—It is found that in general the formation of an anisotropic liquid is conditioned by the presence of atomic groups which influence other physical properties, such as the refractivity, the colour, or the specific rotation.

Whilst ethyl *p*-azoxybenzoate exists between 114° and 121° as liquid crystals, the following esters of *p*-azoxybenzoic acid do not form anisotropic liquids; the temperatures given are the melting points: *Methyl*, 203°; n-*propyl*, 103°; iso*propyl*, 96°; n-*butyl*, 105°; iso*amyl*, 122°; *allyl*, 88—89°; *benzyl*, 147°.

p-Azoxycinnamic acid is prepared by reducing *p*-nitrocinnamic acid with arsenious oxide in aqueous sodium hydroxide solution; its esters, which are prepared by the action of the alkyl iodide or bromide on the dry silver salt, crystallise mostly in golden-yellow needles, the *n*-propyl ester in prismatic plates, and give an orange-red coloration with concentrated sulphuric acid. The following aliphatic esters of *p*-azoxycinnamic acid form liquid crystals; the temperatures given are the first and second melting points between which the anisotropic liquid exists:

Methyl, 219—221°, 254—257°; *ethyl*, 141°, 247—249°; n-*propyl*, 123°, 240—243°; iso*propyl*, 148—150°, 184°; n-*butyl*, 110—111°, 214°; iso*amyl*, 144°, 184—186°; n-*octyl*, 94°, 175°; *cetyl*, 105°, 139—141°; *allyl*, 124°, 234—237°; *carbethoxymethyl*, $OEt\cdot CO\cdot CH_2$, 146—148°, 233—235°; *phenacyl*, 229—231°, 238°.

Benzyl p-*azoxycinnamate* melts directly to the isotropic liquid at 174—175°.

The colourless *tetrabromide*, obtained by the action of bromine on ethyl *p*-ethoxycinnamate, melts without passing through an anisotropic phase at 162°.

p-*Azoxybenzylideneacetophenone*, $C_{30}H_{22}O_3N_2$, is prepared by reduction of *p*-nitrobenzylideneacetophenone with arsenious oxide in aqueous sodium hydroxide solution; it crystallises in small, pointed, orange-yellow leaflets, gives a blood-red colour with concentrated sulphuric acid, and melts to an anisotropic liquid at 211°, changing to the isotropic phase at 213°.

Di-p-*acetoxybenzylidenehydrazone* crystallises in small, yellow plates and melts at 185° and again at 192°. The p-*benzoxy*-derivative crystallises in small, yellow needles or plates and melts at 227° and again about 290°.

The *benzenesulphonyl* and *carbethoxy*-derivatives of di-*p*-hydroxybenzylidenehydrazone melt at 167° and 170° respectively and do not form liquid crystals.

Di-*o*-hydroxybenzylidenehydrazone and its methyl and acetyl derivatives and the corresponding *m*-compounds do not form liquid crystals. Whilst dianisylidenehydrazone passes through an anisotropic liquid phase, the hydrazones of piperonal, vanillin, acetylvanillin, and veratraldehyde and of derivatives of anisaldehyde in which the *p*-methoxy-group is substituted by an amino-, a dimethylamino-, or a nitro-group, when heated melt directly to the isotropic liquid. Under special conditions, the formation of an anisotropic liquid by di-*p*-aminobenzylidenehydrazone and by acetyl-*p*-coumaric acid has been observed.

p-Methoxycinnamic acid, but not its methyl or ethyl ester, forms an anisotropic liquid. G. Y.

***o*-Azoacetanilide.** STEFAN VON NIEMENTOWSKI (*Ber.*, 1906, **39**, 742—744).—The substance, obtained by the author in 1896 by the reduction of *o*-nitroacetanilide with zinc dust and acetic acid, and regarded by him as oxy-β-methylbenziminazole, agrees in all its properties except crystalline form with *o*-azoacetanilide (compare Willstäter and Pfannenstiel, Abstr., 1905, i, 723); the single difference is probably due to the use of different solvents. C. S.

Action of Sodium Hypobromite on Primary Aromatic Amines. WILHELM MEIGEN and E. NOTTEBOHM (*Ber.*, 1906, **39**, 744—747. Compare Abstr., 1900, i, 702).—The behaviour of sodium hypobromite is similar to that of the hypochlorite. ψ-Cumidine is oxidised to azo-ψ-cumene and *p*-aminobenzoic acid to *p*-azobenzoic acid. 5-Aminoquinoline or bromo-5-aminoquinoline (Claus and Schnell, Abstr., 1896, i, 319) is oxidised to *quinolineazine*, $C_{18}H_{10}N_4$, which crystallises in glassy, yellow needles and melts above 420°; the *platinichloride*, $C_{18}H_{10}N_4,H_2PtCl_6$, forms bronze-yellow crystals. The azine is reduced by stannous chloride and hydrochloric acid to a hydrazine, which forms a dark green double salt with stannous chloride and is reconverted into the azine by atmospheric oxygen or warm dilute nitric acid. C. S.

The Relation between Quinonehydrazones and *p*-Hydroxyazo-compounds. III. Quinoneoximehydrazones. WALTHER BORSCHE (*Annalen*, 1905, **343**, 176—207. Compare Abstr., 1905, i, 719).—The hitherto unknown quinoneoximehydrazones are of interest, since they may exhibit a tautomerism with the azo-derivatives of β-phenylhydroxylamine similar to that observed between the quinonehydrazones and the *p*-hydroxyazo-compounds. Since the quinonoid mono-condensation products from quinones and primary hydrazones are not known, the condensation of hydrazines and quinoneoximes is used as a method of preparation. Alkylated hydrazines will not condense with the quinone-oximes, but acylated hydrazines of the types

$$NH_2\cdot NH\cdot COR$$

and $NH_2\cdot NR\cdot COR$ readily combine with quinoneoximes, yielding the oximehydrazones. The products obtained show very different behaviour with respect to their solubility in alkali hydroxides. Alkaline solutions of some of these compounds are readily oxidised by the air, thus:

$$O + 2NHPh\cdot CO\cdot N{:}N\cdot C_6H_4\cdot NH\cdot OH = ON_2(C_6H_4\cdot N_2\cdot CO\cdot NHPh)_2 + 2H_2O.$$

[With H. KÜHL.]—*Quinoneoximebenzoylhydrazone*,

$$OH\cdot N{:}C_6H_4{:}N\cdot NHBz,$$

prepared from benzoquinoneoxime and benzoylhydrazine hydrochloride in dilute alcoholic solution, crystallises in brownish-yellow leaflets melting and decomposing at 209—210°, and is very stable towards alkalis, but oxidised by alkaline oxidising agents; it does not react with hydroxylamine hydrochloride, but is resolved by hydrochloric acid into benzoic acid and *p*-aminophenol, and by sulphuric acid into benzoic acid and phenol; nitric acid converts it into nitrobenzene.

Benzoylbenzoquinoneoximebenzoylhydrazone, $OBz\cdot N{:}C_6H_4{:}N\cdot NHBz$, prepared from benzoylbenzoquinoneoxime and benzoylhydrazine hydrochloride, is a golden-yellow, crystalline powder, melting and decomposing at 196—198°, and is soluble in alcoholic alkali hydroxides. 2-*Toluquinoneoxime-5-benzoylhydrazone*,

$$\mathrm{OH\cdot N{:}C}<\begin{array}{l}\mathrm{CMe{:}CH}\\ \mathrm{CH{=}CH}\end{array}>\mathrm{C{:}N\cdot NHBz},$$

prepared from nitroso-*m*-cresol and benzoylhydrazine hydrochloride, is a yellowish-brown, crystalline powder decomposing at 200—202°. 2-*Benzoylthymoquinone-5-benzoylhydrazone*, prepared from benzoylthymoquinoneoxime and benzoylhydrazine hydrochloride, crystallises in yellowish-white needles melting at 236°. *Benzoyl-α-naphthaquinoneoximebenzoylhydrazone*, $\mathrm{OBz\cdot N{:}C_{10}H_6{:}N\cdot NHBz}$, prepared from benzoyl-α-naphthaquinoneoxime and benzoylhydrazine hydrochloride, crystallises in yellow needles decomposing at 207—208°.

Benzoquinoneoximehippurylhydrazine,

$$\mathrm{OH\cdot N{:}C_6H_4{:}N\cdot NH\cdot CO\cdot CH_2\cdot NHBz},$$

prepared from benzoquinoneoxime and hippurylhydrazine hydrochloride, is a yellowish-white, crystalline powder, melting and decomposing at 219°. 3-*Toluquinoneoxime-6-hippurylhydrazone*,

$$\mathrm{OH\cdot N{:}C_6H_3Me{:}N\cdot NH\cdot CO\cdot CH_2\cdot NHBz},$$

obtained in a similar manner from nitroso-*o*-cresol, is a brown powder at 209°. 2-*Toluquinoneoxime-5-hippurylhydrazone*, similarly prepared from nitroso-*m*-cresol, crystallises in brown scales melting and decomposing at 212°. 2-*Thymoquinoneoxime-5-hippurylhydrazone* is obtained in a similar manner from 2-thymoquinoneoxime, and crystallises in slender, yellow needles decomposing at 240°. α-*Naphthaquinoneoximehippurylhydrazone*, $\mathrm{OH\cdot N{:}C_{10}H_6{:}N\cdot NH\cdot CO\cdot CH_2\cdot NHBz}$, prepared from α-naphthaquinoneoxime, is a yellow powder melting at about 260°.

Quinoneoximephenylsemicarbazone, $\mathrm{OH\cdot N{:}C_6H_4{:}N\cdot NH\cdot CO\cdot NHPh}$, prepared from phenylsemicarbazide hydrochloride and benzoquinoneoxime, crystallises in yellowish-white needles exploding at 217°, and is soluble in alkalis with a reddish-brown coloration. Its *benzoyl* derivative, prepared by benzoylating the hydrazone in pyridine solution, crystallises in insoluble, yellow needles. When air is passed through, or hydrogen peroxide added to the alkaline solution of the hydrazone just mentioned, *azoxybenzene*-4 : 4′-*disazoformanilide*,

$$\mathrm{(NHPh\cdot CO\cdot N{:}N\cdot C_6H_4)_2N_2O},$$

is produced, crystallising in orange-red needles melting and decomposing at 229—230°.

2-*Toluquinoneoxime-6-phenylsemicarbazone*,

$$\mathrm{OH\cdot N{:}C_6H_3Me{:}N\cdot NH\cdot CO\cdot NHPh},$$

prepared from nitroso-*o*-cresol and phenylsemicarbazide hydrochloride, is a brown, crystalline powder decomposing at about 225°. 2-*Toluquinoneoxime-5-phenylsemicarbazone*, prepared from nitroso-*m*-cresol, is a yellow powder exploding at 228—229°. 2-*Thymoquinoneoxime-5-phenylsemicarbazone*, $\mathrm{OH\cdot N{:}C_6H_2MePr^{\beta}{:}N\cdot NH\cdot CO\cdot NHPh}$, prepared from nitrosothymol, crystallises in yellow needles melting at 234°, and insoluble in dilute alkali hydroxides. 3-*Thymoquinoneoxime-6-phenylsemicarbazone*, prepared from nitrosocarvacrol, crystallises in yellow needles melting at 204—205° and is insoluble in dilute alkali hydroxides. α-*Naphthaquinoneoximephenylsemicarbazone*,

$$\mathrm{OH\cdot N{:}C_{10}H_6{:}N\cdot NH\cdot CO\cdot NHPh},$$

forms yellow crystals melting at 242°; it is readily soluble in dilute alkali hydroxides, the solution being oxidised neither by air nor by hydrogen peroxide.

Benzoquinoneoximebenzoylphenylhydrazone, $OH\cdot N:C_6H_4:N\cdot NPhBz$, crystallises in yellowish-green rhombohedra or leaflets melting at 177° and soluble in alkali hydroxides; its alkaline solution is oxidised by the air, *dibenzeneazoazoxybenzene*, $ON_2(C_6H_4\cdot N:NPh)_2$, separating; the latter, which is produced by boiling nitroazobenzene with a sodium methoxide solution, crystallises in orange-yellow needles melting at 218°. On reduction with zinc dust and acetic acid, the benzoquinoneoximebenzoylphenylhydrazone is converted into benzanilide and *p*-phenylenediamine, and when boiled with hydroxylamine hydrochloride in alcoholic solution it yields the dioxime of benzoquinone, and with nitric acid in acetic acid solution *p*-nitroazobenzene.

Benzoylbenzoquinoneoximebenzoylphenylhydrazone, prepared in a similar manner from benzoylbenzoquinoneoxime, crystallises in orange-red leaflets melting at 187—188°, and when warmed with alcoholic potassium hydroxide is converted into dibenzeneazoazoxybenzene. 2-*Benzoyltoluquinoneoxime-5-benzoylphenylhydrazone*,

$$OBz\cdot N:C_6H_3Me:N\cdot NBzPh,$$

occurs in two forms, which are probably stereoisomeric; one crystallises in red needles melting at 190° and the other in leaflets melting at 202°. When warmed with alcoholic potassium hydroxide, it yields 2 : 2′-*dimethyl*-4 : 4′-*dibenzeneazoazoxybenzene*, $ON_2(C_6H_3Me\cdot N:NPh)_2$, crystallising in brown needles melting at 158°. 2-*Benzoylthymoquinoneoxime-5-benzoylphenylhydrazone*, $OBz\cdot N:C_6H_2MePr^{\beta}:N\cdot NBzPh$, prepared from benzoylnitrosothymol, crystallises in orange-yellow leaflets melting at 183° and is converted by boiling with alcoholic potassium hydroxide into 2 : 2′-*dimethyl*-5 : 5′-*diisopropyl*-4 : 4′-*dibenzeneazoazoxybenzene*,

$$ON_2(C_6H_2MePr^{\beta}\cdot N:NPh)_2,$$

which crystallises in dark red needles melting at 147°. K. J. P. O.

Action of Diazohydrates on Oximino-compounds. H. W. Bresler, W. H. Friedemann, and Julius Mai (*Ber.*, 1906, **39**, 876—883. Compare Abstr., 1892, 163, 1079; Bamberger, Abstr., 1899, i, 589).—m-*Tolyldiazobisacetoxime*, $C_{13}H_{20}O_2N_4$, prepared by adding the diazo-solution, obtained from *m*-toluidine, hydrochloric acid, and sodium nitrite, to a solution of acetoxime in aqueous sodium hydroxide, separates from ethyl alcohol in yellow needles and melts at 125°. Its alcoholic solution gives a blue coloration with ferric chloride.

o-*Tolyldiazobisacetoxime*, $C_{13}H_{20}O_2N_4$, prepared in an analogous manner, separates from ether in yellow needles and melts at 89°. It gives a greenish-blue coloration with ferric chloride.

p-*Xylyldiazobisacetoxime*, $C_{14}H_{22}O_2N_4$, prepared from acetoxime and diazo-*p*-xylene hydroxide, separates from light petroleum in yellow needles and melts at 99°. Its alcoholic solution gives a bluish-green coloration with ferric chloride.

m-*Xylyl-4-diazobisacetoxime*, $C_{14}H_{22}O_2N_4$, prepared from *m*-4-xylidine in an analogous manner, separates from a mixture of alcohol and ether in pink leaflets and melts at 87°.

The *compound* $C_{15}H_{21}O_2N_4$, prepared from ψ-cumidine, separates from light petroleum in glistening needles and melts at 98°.

Anisyl-4-diazobisacetoxime, $C_{13}H_{20}O_3N_4$, prepared from *p*-anisidine, separates from methyl alcohol in glistening, nacreous crystals and melts at 125°. With ferric chloride, it forms a greenish-blue coloration, which quickly becomes violet.

Phenetyl-4-diazobisacetoxime, $C_{14}H_{22}O_3N_4$, prepared from *p*-phenetidine, melts at 125—127°.

The *compound* $C_{13}H_{18}O_4N_4$, prepared from *p*-aminobenzoic acid, is a yellowish-white solid; its *silver* salt is yellow.

Phenyldiazobismethylethylketoxime, $C_{14}H_{22}O_2N_4$, prepared by the addition of a diazotised aniline solution to methylethylketoxime, separates from 75 per cent. alcohol and melts at 95°. Its alcoholic solution gives a bluish-green coloration with ferric chloride.

p-*Nitrodiazobenzeneimide*, $C_6H_4O_2N_4$, prepared from methyl ethyl ketoxime and diazotised *p*-nitroaniline, separates from aqueous methyl alcohol in glistening leaflets and melts at 71°.

Phenyldiazobisdiethylketoxime, $C_{16}H_{26}O_2N_4$, prepared from diazobenzene chloride and diethylketoxime, separates from aqueous methyl alcohol in glistening crystals and melts at 55°. With ferric chloride it gives a greenish-blue coloration, which quickly becomes green.

The *compound* $C_{13}H_{20}O_2N_4$, prepared from propaldoxime and *p*-diazotoluene hydroxide, separates from light petroleum in colourless crystals and melts at 74°.

Benzenediazobis-4-dimethylaminobenzaldoxime, $C_{24}H_{28}O_2N_6$, prepared from diazobenzene hydroxide and *p*-dimethylaminobenzaldoxime, separates from a mixture of chloroform and methyl alcohol in yellow needles and melts at 183—185°.

p-*Toluenediazobis-4-dimethylaminobenzaldoxime*, $C_{25}H_{30}O_2N_6$, prepared from diazotised *p*-toluidine and *p*-dimethylaminobenzaldoxime, separates from a mixture of chloroform and methyl alcohol in yellow needles and melts at 167°.

Anisole-4-diazobis-4-dimethylaminobenzaldoxime, $C_{25}H_{30}O_3N_6$, prepared from diazotised *p*-anisidine and *p*-dimethylaminobenzaldoxime, crystallises from benzene in yellow needles and melts at 162°.

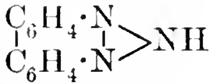
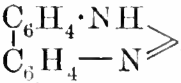
The introduction of positive groups into the oximes used induces the combination with diazohydroxides to take place more readily. Negative groups have the opposite effect. Stable compounds were obtained only with the lower members of homologous series. A. McK.

[Azo-dyes from 3:4:6-Trichloroaniline.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 161922. Compare this vol., i, 121).—The diazonium compound of 3 : 4 : 6-trichloroaniline combines with sodium β-naphthol-3 : 6-disulphonate to form an azo-dye which yields fast bluish-red lakes. The corresponding compound from 2 : 4 : 6-trichloroaniline is quite different in character. C. H. D.

[Azo-dyes from Nitro-*m*-phenylenediaminesulphonic Acid.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 161277).—Azo-compounds, yielding fast yellow or orange lakes, are obtained by combining diazosulphonic acids of the benzene or naphthalene series with nitro-*m*-phenylenediamine-sulphonic acid. These lakes resist light better than the corresponding compounds from nitro-*m*-diamines (Abstr., 1905, i, 251). This behaviour is exceptional, as an increase in the number of sulphonyl groups usually renders such compounds less suitable for the production of insoluble lakes. C. H. D.

Azo-dyes from Aminoanthraquinonesulphonic Acids. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 161151).—Azo-dyes, yielding fast, yellowish-red to bluish-red lakes, are obtained by combining diazotised 1-aminoanthraquinone-2- or -6-sulphonic acid or 1 : 5-diaminoanthraquinone-2 : 6-disulphonic acid with *α*- or *β*-naphthol-3 : 6-disulphonic acid. C. H. D.

[1-Hydroxy-4-diazoanthraquinone.] Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 161954).—In the oxidation of anthraquinone to quinizarin by means of sulphuric acid and sodium nitrate in presence of boric acid and mercury sulphate, an intermediate product, 1-*hydroxy*-4-*diazoanthraquinone sulphate*, is formed at 120—150°. On cooling and adding sodium hydroxide, the *diazo*-compound is precipitated in reddish-brown crystals and may be purified by dissolving in dilute sulphuric acid and precipitating with sodium acetate. Warming with alcohol converts it readily into erythroxyanthraquinone; heating with sulphuric acid at 180° converts it into quinizarin. C. H. D.

Tri-imides or Azoimides of the Benzidine Series. Wilhelm Vaubel and Otto Scheuer (*Zeit. Farb. Text. Ind.*, 1906, 5, 61—62. Compare Vaubel, Abstr., 1900, i, 615; 1903, i, 299).—The action of 1 mol. of nitrous acid on 1 mol. of benzidine hydrochloride in neutral or acid solution at 10—15° leads to the formation of the azoimide or diazoamino-compound,  $\begin{array}{l}C_6H_4\cdot N\\ | \qquad\ \ |\\ C_6H_4\cdot N\end{array}\!\!>NH$ or  $\begin{array}{l}C_6H_4\cdot NH\\ |\\ C_6H_4-N\end{array}\!\!\geqslant N$, which, on treatment with an excess of hydrochloric acid, is converted into 4-aminodiphenyl-4′-diazonium chloride, $NH_2\cdot C_6H_4\cdot C_6H_4\cdot N_2Cl$.

Similar derivatives are obtained from tetrabromobenzidine, tolidine, dibromotolidine, diaminostilbene, diphenetidine, and dianisidine. The azoimides are greyish-brown to brown powders, have no sharp melting point, but decompose and evolve nitrogen at high temperatures, forming at least two decomposition *products*. G. Y.

Preparation of Sulphineazo-compounds. Gesellschaft für Chemische Industrie in Basel (D.R.-P. 161462).—4-Chloro-1 : 3-dinitrobenzene condenses with potassium thiocyanate, and the product when reduced yields 2 : 2′-*dinitro*-4 : 4′-*diaminodiphenyl disulphide*, $S_2[C_6H_3(NO_2)\cdot NH_2]_2$. The tetrazonium derivative of this combines with phenols, aromatic amines, pyrazolone derivatives, &c., to form *sulphine-azo*-dyes, all of which may be reduced by sodium sulphide to compounds having the constitution $SNa\cdot C_6H_3(NO_2)\cdot N\colon N\cdot X$. When the component used for the preparation of the azo-compound does not contain either a carboxyl or a sulphonyl group, and is therefore insoluble in alkalis, it is possible in this way to obtain a soluble product. Air, air and steam, or oxidising agents re-form the insoluble disulphide, metallic salts form insoluble mercaptides, and it is therefore possible to fix the dyes on the fibre. A table of the shades obtained by the use of different components is given. C. H. D.

Polyazo-compounds. KALLE & CO. (D.R.-P. 161720).—Diazonium salts of the general formula $R\cdot N:N\cdot C_6H_4\cdot N_2\cdot Cl$, where R is a phenol, amine, or diamine residue prepared from *p*-phenylenediamine, combine in alkaline solution with 1-*p*-aminobenzeneazo-2-amino-5-naphthol-7-sulphonic acid to form dyes of the general formula

$$R\cdot N:N\cdot C_6H_4\cdot N:N\cdot C_{10}H_3(NH_2)(OH)(SO_3H)\cdot N:N\cdot C_6H_4\cdot NH_2,$$

which dye fast blue shades. C. H. D.

Amino-acids, Polypeptides, and Proteids. EMIL FISCHER (*Ber.*, 1906, **39**, 530—610).—A lecture delivered before the German Chemical Society. G. Y.

Yield of Glutamic Acid from Various Proteids. THOMAS B. OSBORNE and RALPH D. GILBERT (*Amer. J. Physiol.*, 1906, **15**, 333—356).—The amount of glutamic acid yielded by various proteids, mainly of vegetable origin, is given. A few quantitative determinations of other products are given also. The object of the research was to find a logical basis for the use of one form of proteid rather than others in nutrition, in health and disease. In animal proteids, the yield of glutamic acid per cent. varies from 7 to 10. In vegetable proteids, with one exception (leucosin of wheat, 5·7 per cent.), the yield is larger (12 to 37 per cent.). W. D. H.

Ovo-vitellin. LOUIS HUGOUNENQ (*Compt. rend.*, 1906, **142**, 173—175).—The various amino-acids obtained by the hydrolysis of vitellin were estimated. The small yield of glycine resembles that from caseinogen, a very similar proteid both as regards its composition and its function as a tissue-forming substance in early life.

W. D. H.

Union of Carbon Dioxide with Amphoteric Amino-substances. II. MAX VON SIEGFRIED (*Zeit. physiol. Chem.*, 1905, **46**, 401—414. Compare Abstr., 1905, ii, 332).—The proteids of blood serum, when acted on by carbon dioxide in presence of calcium hydroxide, form calcium salts of proteid carbamic-acids. The preparation and analysis of the pure *calcium* salts of carbamo-succinic and -glutaric acids and of asparagine-, lysine-, and arginine-carboxylic acids is described. It is shown that alanine and glycine are converted by carbon dioxide in aqueous solution into the corresponding carbamic acids. E. F. A.

Crude Gluten. F. A. NORTON (*J. Amer. Chem. Soc.*, 1906, **28**, 8—25).—Crude gluten contains about 75 per cent. of pure gluten gliadin and glutenin) and small amounts of non-gluten proteid, mineral matter, fat, starch, and fibre. Its relation to the total proteid (N × 5·7) varies in different flours, the amount being greater than that of total proteid in low-grade flours, nearly the same in patent flours, and less in whole wheat meal.

The determination of crude gluten is of little use in the valuation of flours. The best simple method for estimating the gluten content and ascertaining the character of the gluten seems to be the determination of total and gliadin nitrogen with expression of the ratio of gliadin to total proteid (N × 5·7). N. H. J. M.

Separation of the Phosphorus from Caseinogen by Enzymes and Alkali. R. H. Aders Plimmer and William M. Bayliss (*J. Physiol.*, 1906, **33**, 439—461).—Trypsin converts the whole of the phosphorus of caseinogen into a soluble form in twenty-four hours, except for a small insoluble residue derived partly from the trypsin and partly from the caseinogen, and consisting probably of decomposition products of nucleo-proteid. The curve for the rate of separation of the phosphorus runs parallel to that for the increase in electrical conductivity for the first eight hours; then it is less rapid. The soluble phosphoric acid consists of inorganic phosphoric acid (35 per cent.) and an organic compound (65 per cent.). Pepsin produces a similar change, but exceedingly slowly. Papain, acting best in a neutral or faintly acid medium, is intermediate in the rate at which it acts. Ovo-vitellin containing lecithin is digested slowly as compared with caseinogen. One per cent. sodium hydroxide resembles trypsin in its rate of action, and the product is wholly inorganic phosphoric acid. The organic compound of phosphorus obtained by tryptic action is not completely converted into inorganic phosphoric acid by 1 per cent. sodium hydroxide. The total quantity of inorganic phosphoric acid obtained by the successive use of the two reagents is 50 per cent. of the total phosphorus of the caseinogen. W. D. H.

Jecorin. Max Siegfried and H. Mark (*Zeit. physiol. Chem.*, 1905, **46**, 492—495).—Jecorin is regarded as being a definite substance, and not a mixture, as Meinertz states (this vol., i, 124). W. D. H.

Composition of "Dichromated" Gelatin which has Spontaneously become Insoluble in the Dark. Auguste Lumière, Louis Lumière, and Alphonse Seyewetz (*Bull. Soc. chim.*, 1906, [iii], **35**, 14—16. Compare Abstr., 1905, i, 847, 848).—Films of gelatin spread on glass were treated with a 3 per cent. solution of potassium dichromate while exposed in the dark, at ordinary temperatures or at 120°, until they had become insoluble in water at 80°. They were then washed and analysed.

The films prepared at the ordinary temperature were exposed for one, two, or four and half months; they contained 0·67, 0·93, and 1·15 per cent. of chromium sesquioxide, and 1·19, 0·46, and 0·22 per cent. of ash respectively, but did not contain any chromium trioxide.

The films prepared at 120° were exposed in the dark for one and six days, and contained 0·54 and 2·72 per cent. of chromic acid, 8·68 and

20·59 per cent. of chromium sesquioxide, and 0·06 and 0·1 per cent. of ash respectively.

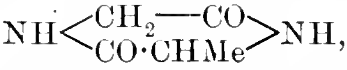
The results show that "insoluble gelatin," prepared in the dark at the ordinary temperature, contains smaller quantities of chromium sesquioxide than that produced by exposure to light (*loc. cit.*), and is also less resistant to the action of boiling water. That prepared at 120° in the dark is quite insoluble in boiling water, but is broken up by it into small fragments, and, like "insoluble gelatin" prepared by exposure to light, appears to contain some uncombined chromium sesquioxide, produced by direct reduction of the dichromate by the gelatin.

Similar experiments made with films of gelatin on paper gave unsatisfactory results owing to the difficulty of entirely removing the paper before analysis.

T. A. H.

Formation of a Dipeptide by Hydrolysis of Silk Fibroin.

Emil Fischer and Emil Abderhalden (*Ber.*, 1906, **39**, 752—760. Compare Abstr., 1903, i, 694).—The successive hydrolysis of silk fibroin by sulphuric acid and pancreatin yields tyrosine and a syrup containing amino-acids, di- and poly-peptides. The dipeptides were isolated in the following way. The syrup, dissolved in alcohol, was esterified by hydrogen chloride, and the solution, after removal of the mineral acid by sodium ethoxide, was evaporated below 65° under 10 mm. pressure, the distillate containing a small quantity of ethyl aminoacetate. The residual greenish-brown syrup was dissolved in alcohol and treated in the cold with dry ammonia, whereby *diketomethylpiperazine*,



$NH<\begin{array}{c}CH_2\text{——}CO\\CO\cdot CHMe\end{array}>NH$, and a small quantity of glycine-tyrosine anhydride were precipitated, the former being finally obtained pure in the form of small needles. It resembles *i*-glycine-alanine anhydride (Abstr., 1903, i, 608), except that it has $[\alpha]_D$ $-3·9°$ at 20°. It is hydrolysed by hydrochloric acid, forming glycine and *d*-alanine, and by treatment with sodium hydroxide at the ordinary temperature forms a dipeptide which is probably a mixture of glycyl-*d*-alanine and *d*-alanylglycine. It does not depress the melting point of synthetical glycine-*d*-alanine anhydride, with which it is identical, but has a smaller rotatory power, due to the partial racemisation which occurs during the hydrolysis of silk fibroin by sulphuric acid. A better yield of the compound is obtained when the complex products of the hydrolysis are removed by means of phosphotungstic acid before esterification. The hydrolysis of silk fibroin with hydrochloric acid of sp. gr. 1·19 gives a 12 per cent. yield of diketomethylpiperazine, and shows that the formation of this compound is not due to the action of the pancreatin. Experiments were successfully performed which indicate that the production of the compound is not due to a secondary reaction between the primarily formed glycine and *d*-alanine.

C. S.

Crystalline Urinary Albumose. II.

Alide Grutterink and C. J. Weevers de Graaff (*Zeit. physiol. Chem.*, 1905, **46**, 472—481).—The Bence-Jones proteid, which sometimes is obtainable in crystalline

form from urine, is regarded as more akin to a native proteid than to an albumose. It yields, on digestion, products analogous to those obtainable from albumin.
W. D. H.

Peptone. II. LYMAN B. STOOKEY (*Proc. Amer. Physiol. Soc.*, 1905, xii—xiii; *Amer. J. Physiol.*, **15**).—A preliminary statement in regard to a fraction obtained by benzoyl chloride, but the findings are not regarded as conclusive.
W. D. H.

Proteid Peptone. LYMAN B. STOOKEY (*Beitr. chem. Physiol. Path.*, 1906, **7**, 590—595).—From the products of peptic digestion of blood-albumin, benzoyl, benzenesulphonyl, and naphthalenesulphonyl products of peptone were separated. The composition and reactions of these are compared, but, owing to the necessity of abandoning the work prematurely, the products were not defined with necessary exactitude.
W. D. H.

Comparison of Ferments and Lysins. E. W. AINLEY WALKER (*Proc. Physiol. Soc.*, 1905, xxi—xxiv; *J. Physiol.*, **33**).—Examples are given which support the provisional view that ferments are double substances, consisting of a specific amboceptor and a non-specific kinase or complement. Bacteriolysis and similar phenomena are thus to be regarded as special cases of a general physiological reaction.
W. D. H.

Influence of Reaction on the Activity of Amylase. LÉON MAQUENNE and EUGÈNE ROUX (*Compt. rend.*, 1906, **142**, 124—129).—The optimum reaction at which amylase acts on various kinds of starch is that of exact neutrality. Starch solutions and solutions of amylase from malt are usually alkaline, so that enough acid (sulphuric or hydrochloric) must be added to neutralise both, helianthin being used as indicator. The sugar formed is wholly maltose.
W. D. H.

Influence of the Reaction of the Medium on the Activity of Diastases. AUGUSTE FERNBACH (*Compt. rend.*, 1906, **142**, 285—286).—In experiments on the action of very small amounts of amylase on an excess of starch, it was found that the action was quickest under conditions of neutrality to helianthin. The results of Maquenne and Roux, indicating that an alkaline reaction is most favourable [compare, however, preceding abstract], is attributed to a large excess of malt extract and a small amount of starch having been employed.
N. H. J. M.

Action of Invertin in a Heterogeneous Medium. VICTOR HENRI (*Compt. rend.*, 1906, **142**, 97—100).—The rate of the inversion of sucrose by a mixture of gelatin and invertin, separated from the sucrose solution by a thin layer of pure gelatin, is nearly proportional to the strength of the sucrose solution. When, however, the invertin is present in the solution itself, the inversion is about the same in the two solutions of different strengths. Variations in temperature have much less effect on the inversion of sucrose when the invertin is mixed with gelatin than when it is present in the solution.

The concentration of substances transformed by the ferment will influence the rate of digestion when the ferments are endocellular, but not when they are distributed in the liquids of the organism.

N. H. J. M.

Enzyme Action. II. H. P. Barendrecht (*Zeit. physikal. Chem.*, 1906, **54**, 367—375).—The conversion of lactose into galactose and dextrose by the action of lactase (obtained from *Saccharomyces kephir*) has been studied on the lines of the author's earlier work (Abstr., 1904, ii, 551, 719). The conversion is retarded twice as much by galactose as by dextrose, and about as much by a molecule of lævulose as by a molecule of galactose and a molecule of dextrose together.

It is found that the inversion of sucrose by invertase, obtained from kephir yeast, is less retarded by dextrose, lævulose, and galactose than inversion by invertase obtained from ordinary yeast.

In confirmation of Brown's observation (Trans., 1902, **81**, 382), the author finds that lactose exerts practically no retarding influence on the inversion of sucrose by ordinary invertase, a result which is interpreted in terms of the theory previously brought forward (*loc. cit.*).

Emphasis is laid on the fact, demonstrated by the author's work, that the action of enzymes on bioses is retarded much less by the hexoses produced in the reaction than by other hexoses. J. C. P.

Action of Lipase. Arthur S. Loevenhart (*Proc. Amer. Physiol. Soc.*, 1905, xxvii—xxviii; *Amer. J. Physiol.*, **15**).—The substance in liver extracts which Magnus termed the co-ferment of lipase is bile salts. Observations also show that the enzyme lipase is probably different from that which causes hydrolysis of esters. But the existence of such an enzyme, esterase, is to be considered in a later paper.

W. D. H.

Action of Papain. C. Delezenne, H. Mouton, and E. Pozerski (*Compt. rend.*, 1906, **142**, 177—179).—Papain acts best in a slightly acid medium, and forms from albumin the usual proteolytic products. The action follows the law of square roots formulated by Schütz. In some prolonged experiments, an increase of coagulable proteid occurs in the later stages of digestion, a phenomenon regarded as indicating a reversible action, or due to the formation of plasteins. W. D. H.

Pancreas Steapsin and the Velocity of Fat Hydrolysis produced by Enzymes. Aristides Kanitz (*Zeit. physiol. Chem.*, 1905, **46**, 482—491).—A steapsin extract, prepared by digesting an ox or pig's pancreas for a considerable time with glycerol, brings about the rapid hydrolysis of olive oil. This change follows the law $x/\sqrt{t} =$ a constant; x being the amount hydrolysed in time t.

The cases studied by Connstein, Hoyer and Wartenberg (Abstr., 1903, i, 218) and by Zellner (Abstr., 1905, ii, 550) are shown to obey the same law.

E. F. A.

Organic Chemistry.

The Series C_nH_{2n-2} in Louisiana Petroleum. Charles E. Coates (*J. Amer. Chem. Soc.*, 1906, 28, 384—388. Compare Coates and Best, Abstr., 1905, ii, 833).—The crude oil from Jennings, which is the lightest Louisiana petroleum, contains a small proportion of saturated hydrocarbons of comparatively low molecular weight, which have an odour resembling that of turpentine but are optically inactive. The following hydrocarbons were separated by repeated fractional distillation. The *hydrocarbon*, $C_{10}H_{18}$, boils at 168—170° under 760 mm. pressure, has a sp. gr. 0·8146 at 22°/4°, and n_D 1·4460 at 25°. The *hydrocarbon*, $C_{11}H_{20}$, boils at 198—200° under 760 mm. pressure, has a sp. gr. 0·8378 at 26°/4°, and n_D 1·4582 at 25°. The *hydrocarbon*, $C_{12}H_{22}$, boils at 215—217° under 760 mm. pressure, has a sp. gr. 0·8511 at 28°/4°, and n_D 1·4640 at 25°. The *hydrocarbon*, $C_{13}H_{24}$, boils at 235—238° under 760 mm. pressure, has a sp. gr. 0·8629 at 22°/4°, and n_D 1·4692 at 25°.

Small fractions were obtained which probably consisted of the hydrocarbons C_8H_{14} and C_9H_{18}. The former boiled at 120·5°, had a sp. gr. 0·7747 at 24°/4°, and n_D 1·4260 at 25°. The latter boiled at 145·7°, had a sp. gr. 0·7992 at 24°/4°, and n_D 1·4370 at 25°. E. G.

The Alcoholic Function. Louis Henry (*Bull. Acad. roy. Belg.*, 1905, 537—554. Compare this vol., i, 133).—It is pointed out that, by reason of their great reactivity with the halogen acids, acid anhydrides, and acid chlorides, the tertiary alcohols should be regarded as the organic analogues of potassium hydroxide, whilst the primary and secondary alcohols in their behaviour with these reagents more closely resemble water.

Thus the secondary alcohol, methyl*tert*.butylcarbinol, is converted completely by acetyl chloride into the acetate, which boils at 143° under 757 mm. pressure. Its isomeride, dimethyl*iso*propylcarbinol, on the contrary, with the same reagent yields acetic acid and dimethyl*iso*propyl chloride. When a mixture of equal quantities of trimethylcarbinol and *iso*butyl alcohol is saturated with hydrogen chloride at atmospheric temperature, the former alcohol is converted into the corresponding chloride, but the latter is not acted on. The results of a number of similar experiments are quoted, illustrating the author's contention. T. A. H.

Formation of Alcoholates by Certain Salts in Solution in Methyl and Ethyl Alcohols. Harry C. Jones and LeRoy McMaster (*Amer. Chem. J.*, 1906, 35, 316—326. Compare Jones and Getman, Abstr., 1904, ii, 386, 711).—The molecular elevation of the boiling point of methyl alcohol produced by lithium chloride, bromide, and nitrate has been determined. The results are tabulated and lead to the conclusion that alcoholates are formed in the solutions, and that as the concentration of the solution becomes greater a larger proportion of alcohol is held in combination and the molecular rise in boiling point therefore increases.

Determinations have also been made of the molecular elevation of the boiling point of ethyl alcohol brought about by lithium chloride, bromide, and nitrate, and calcium nitrate. The results obtained confirm those of Jones and Getman (Abstr., 1904, ii, 711).

E. G.

Rise of Temperature when Chloroform and Ethyl Ether are Mixed. Leopold Rosenthaler (*Arch. Pharm.*, 1906, **244**, 24—25).—When 59·5 grams of chloroform and 37·0 grams of ethyl ether, both at 15·2°, are mixed, the temperature of the mixture rises to 30·2°.

C. F. B.

Thiocarbonates. B. Holmberg (*J. pr. Chem.*, 1906, [ii], **73**, 239—248. Compare Abstr., 1905, i, 323).—The action of carbon dioxide on potassium hydrogen sulphide in alcoholic solution leads to the formation of hydrogen sulphide and a mixture of potassium hydrogen carbonate and potassium ethyl carbonate, which, contrary to Chancel's statement (*Jahresb.*, 1851, 513), are formed also by the interaction of carbon dioxide and potassium ethyl mercaptide in alcoholic solution.

The action of carbonyl sulphide on potassium hydrogen sulphide in alcoholic solution leads to the formation of hydrogen sulphide and potassium ethyl thiocarbonate, which is formed also by the interaction of carbonyl sulphide and potassium ethyl mercaptide in alcoholic solution. On the other hand, the action of carbonyl sulphide on potassium ethyl mercaptide in aqueous solution leads to the liberation of the mercaptan and formation of potassium hydrogen carbonate.

The author confirms his statement, in opposition to Biilmann (*Diss.*, Copenhagen, 1904, 1905), that the action of carbon disulphide on potassium hydrogen sulphide in alcoholic solution leads to the formation of potassium trithiocarbonate, potassium xanthate, and hydrogen sulphide.

Potassium ethyl trithiocarbonate, formed by the action of carbon disulphide on potassium ethyl mercaptide in alcoholic solution, crystallises in intensely yellow, stout needles or prisms (compare Chancel; *loc. cit.*), and, on addition of hydrochloric acid, yields ethyl hydrogen trithiocarbonate as a heavy, red oil of unpleasant odour.

When boiled in neutral or alkaline solution, trithiocarbodiglycollic acid yields thioglycollic acid and ammonium thiocyanate, and not thiocarbamide, as stated previously (*loc. cit.*). G. Y.

Fatty Acids of Brain Lecithin. H. Cousin (*J. Pharm. Chim.*, 1906, [vi], **23**, 225—230).—The lecithin was isolated from cow brains by a modification of Thudichum's process, and was saponified by heating with a solution of sodium hydroxide in alcohol. The method of separating and identifying the fatty acids used was the same as that previously employed (Abstr., 1903, i, 675). Stearic, palmitic, and oleic acids were identified. In addition, an oily acid was obtained, having an iodine value 129; this is being studied further and may prove to be linoleic acid. Choline and glycerophosphoric acid were also found among the hydrolytic products. T. A. H.

Composition of Lecithins. M. Wintgen and O. Keller (*Arch. Pharm.*, 1905, **244**, 3—11).—Samples of lecithins of different origin gave the following results on analysis :

	N per cent.	P per cent.	Ratio N : P.
Distearyl-lecithin (calculated)	1·73	3·81	1 : 2·22
Coml. lecithin from yolk of egg	2·25	3·49	1 : 1·55
,, ,, purified	2·37	3·78	1 : 1·59
Egg-lecithin, prepared by authors :			
from ethereal extract	2·50	3·69	1 : 1·48
from alcoholic extract	2·51	3·57	1 : 1·52
Lecithin, prepared by authors :			
from brown Soja beans	1·90	2·96	1 : 1·56
from black Soja beans	1·84	2·51	1 : 1·27

C. F. B.

Electrolysis of the Alkali Salts of Organic Acids. IV. Julius Petersen (*Zeit. Elektrochem.*, 1906, **12**, 141—145. Compare Abstr., 1898, i, 352, and 1900, ii, 522).—When a solution of the potassium salt of α-methylbutyric acid is electrolysed, the products are trimethylcarbinyl α-methylbutyrate, $\gamma\delta$-dimethylhexane, Δ^{β}-butylene ($CH_3\cdot CH:CH\cdot CH_3$), carbon dioxide, hydrogen, and a little oxygen. The quantity of butylene increases as the current density increases, and also as the solution becomes more dilute.

When electrolysed in a warm dilute alcoholic solution, potassium laurate yields, mainly, the hydrocarbon docosane ($C_{22}H_{46}$) and small quantities of ethyl laurate. Myristic, palmitic, and stearic acids behave in the same way, yielding a hexacosane, $C_{26}H_{54}$, melting at 56·6° (89·1 per cent. of the theoretical quantity), *triacontane*, $C_{30}H_{62}$, melting at 66·1° (88·1 per cent.), and *tetratriacontane*, $C_{34}H_{70}$, melting at 72·9° (73·6 per cent.) respectively. T. E.

Reagent in the Chemistry of Fats. Ernest Twitchell (*J. Amer. Chem. Soc.*, 1906, **28**, 196—200).—Sulphophenyl- and sulphonaphthylstearic acids (Abstr., 1900, i, 296) are found to act as catalytic agents in the hydrolysis of fats. If 1 per cent. of sulphonaphthylstearic acid is boiled with a mixture of fat and water, an almost complete separation of the glycerol is effected in eight to ten hours. A comparison of the hydrolysing power of *N*/75 sulphonaphthylstearic acid and *N*/75 hydrochloric acid on triacetin has shown that these acids are equally effective, but that if an insoluble glyceride is substituted for the triacetin, the hydrochloric acid has practically no effect, whilst the sulphonaphthylstearic acid acts at approximately the same rate as it does on the soluble esters. The property of these sulphostearic acids of dissolving in both fatty acid and water and rendering them mutually soluble has been applied to the separation of solid and liquid fatty acids. E. G.

Ethyl Tetrolate. FRANZ FEIST (*Annalen*, 1906, **345**, 100—116).—Attempts have been made to ascertain whether the acetylene linking of ethyl tetrolate, $CH_3\cdot C\vdots C\cdot CO_2Et$, will bring about condensations of the methyl group with ketone groups in the presence of sodium ethoxide. Although the ester is very reactive, no simple condensation products could be obtained.

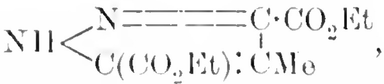
Tetrolic acid was prepared by a modification of Desprez's method. *Ethoxycrotonic acid*, $OEt\cdot CMe\vdots CH\cdot CO_2H$, was obtained as a by-product; it formed leaflets melting at 141°, and when boiled with water was decomposed with the elimination of carbon dioxide. Ethyl tetrolate could be prepared by the usual method; the use of phosphorus pentachloride to form the acid chloride, which might then be used for obtaining the ester, leads to the production of chlorocrotonic acids.

Benzaldehyde and ethyl tetrolate react readily in the presence of sodium, giving the *substance* $(C_9H_8O_2)_x$, which melts and decomposes at 125°; it is not ethyl benzylidenetetrolate. Acetophenone and ethyl tetrolate yield an oil which is possibly the *compound* $COPh\cdot CH_2\cdot CO\cdot C\vdots CMe$. Ethyl acetoacetate is the only product of the action of ethyl tetrolate and ethyl oxalate which could be isolated.

Ethyl tetrolate does not react with sodamide, but in the presence of this reagent yields sodium salts with acetone, acetophenone, and ethyl oxalate. The condensation products could not be isolated; an attempt to couple the product obtained when ethyl oxalate was used with *p*-nitrophenylhydrazine gave a complex *substance*, $C_{17}H_{19}O_7N_3$, which is a yellow powder melting and decomposing at 74° and soluble in alkali hydroxides with a violet coloration.

With a concentrated aqueous or alcoholic solution of ammonia, ethyl tetrolate yields ethyl β-aminocrotonate, but with dilute solutions of ammonia, tetrolamide, $CMe\vdots C\cdot CO\cdot NH_2$, is formed. It was obtained as white crystals from water, melting at 147—148°. With *p*-nitrophenylhydrazine in the presence of mercuric chloride, 1-*p*-nitrophenyl-3-methylpyrazolone (m. p. 214°) is formed, and with benzenediazonium chloride in the presence of sodium acetate, *phenylazoacetoacetamide*, $NPh\vdots NC\cdot HAc\cdot CO\cdot NH_2$, crystallising in needles melting at 145°. Ethyl tetrolate and piperidine yield *ethyl piperidinocrotonate*, which is a syrup giving a violet coloration with ferric chloride in alcoholic solution, and decomposes, yielding the piperidide of tetrolic acid, which melts at 238°. With aniline, ethyl tetrolate seems to form an anilide, which then combines with water producing acetoacetanilide, which reacts with the excess of aniline, yielding acetone and diphenylcarbamide.

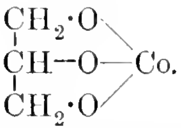
Ethyl tetrolate and phenylhydrazine react in solution in high boiling petroleum, yielding 1-*phenyl*-3-*methyl*-5-*pyrazolone*, which forms crystals melting at 127°, and is converted by ferric chloride into pyrazole-blue; at the same time, bisphenylmethylpyrazolone is formed by the action of the pyrazolone with excess of phenylhydrazine: it is not molten at 320°; this reaction would indicate that the ethyl tetrolate and phenylhydrazine first form the phenylhydrazone of ethyl acetoacetate. Ethyl tetrolate and ethyl diazoacetate react at 140°, yielding the condensed additive product, *ethyl* 4-*methylpyrazole*-3:5-

dicarboxylate, 
$NH<\begin{matrix}N{=\!=\!=}C\cdot CO_2Et \\ C(CO_2Et):CMe\end{matrix}$, which melts at 101°, or, when anhydrous, at 106—107°, and can be hydrolysed to the corresponding acid (melting and decomposing at 305°). K. J. P. O.

l-Lactic Acid. ÉMILE JUNGFLEISCH and MARCEL GODCHOT (*Compt. rend.*, 1906, **142**, 515—518).—l-Lactic acid was prepared from quinine l-lactate (Abstr., 1904, i, 645) through the zinc salt by the process already described (Abstr., 1905, i, 318). Zinc l-lactate closely resembles zinc d-lactate in appearance, has similar solubilities, and approximately the same specific rotations, in an opposite sense, for the same concentrations of solution. l-Lactic acid crystallises in flattened prisms similar to those formed by the dextro-acid, is very hygroscopic, melts at 26—27°, and has a specific rotation which diminishes with increasing dilution of the solution. The specific rotations observed are practically equal to those of the *dextro* acid, but are of opposite sign. The *lævo* acid, like the dextro and racemic isomerides, changes spontaneously in concentrated solutions, forming l-lactyl-lactic acid (Abstr., 1905, i, 259), which is dextrorotatory. This explains the change in the sign of the rotation of l-lactic acid when an aqueous solution is evaporated (compare Abstr., 1905, i, 630). l-Lactyl-lactic acid is reconverted into l-lactic acid when its aqueous solution is heated in a closed tube at 100° for several hours. It is pointed out that Mackenzie (Trans., 1905, **87**, 1373) is in error in assuming that Jungfleisch has withdrawn his statement (Abstr., 1904, i, 796) that l-lactic acid is more readily raçemised than d-lactic acid (compare Abstr., 1905, i, 319). T. A. H.

The Lactide of l-Lactic Acid. ÉMILE JUNGFLEISCH and MARCEL GODCHOT (*Compt. rend.*, 1906, **142**, 637—639. Compare Abstr., 1905, i, 259, 318, 630).—When anhydrous l-lactic acid is distilled at 150—155°, a mixture of l- and i-lactides is obtained, from which the two constituents are readily separated by fractional crystallisation from ether. l-*Lactide* forms orthorhombic crystals enantiomorphously related to the d-lactide crystals (Wyrouboff), whilst in respect of melting point, boiling point, and solubility the two isomerides are identical. l-Lactide is dextrorotatory, and the rotation diminishes as the dilution is increased; solutions containing 0·8158 gram, 0·4079 gram, or 0·2039 gram per 100 c.c. of benzene have $[\alpha]_D$ $+281·6°$, $+268°$, or $+231°$ respectively at 16°. l-Lactide undergoes progressive hydrolysis in contact with cold water, forming l-lactyl-lactic acid and l-lactic acid: thus a solution of 0·1422 gram of l-lactide in 30 c.c. of water immediately after solution and after 2, 6, 12, 18, 42, 66, and 80 hours has $[\alpha]_D + 204°$, $+140°$, $+114°$, $+91°$, $+42°$, $+35°$, $+28°$, and $+14°$ respectively at 12°. i-Lactide is readily obtained by mixing equivalent quantities of l- and d-lactide in ethereal solution. M. A. W.

Tervalent Cobalt and Nickel. STANLEY R. BENEDICT (*J. Amer. Chem. Soc.*, 1906, **28**, 171—177).—A solution of cobaltioxalic acid, $H_6Co_2(C_2O_4)_6$, can be obtained by boiling a solution of a cobalt salt with sodium peroxide, collecting and washing the black cobaltic hydroxide, and dissolving it by pouring a cold saturated solution of oxalic acid on it whilst still on the filter. When this solution is left for a few hours its colour changes from green to pink, and cobaltous oxalate is precipitated. This reduction is only slightly accelerated by sulphurous acid or hydrogen sulphide. If the solution is made alkaline with sodium carbonate, it is not appreciably reduced by boiling, and does not appear to be affected by ferrous salts or stannous chloride. The *calcium* salt crystallises in dark green needles with $6H_2O$, and is very stable towards reducing agents. A method is described for the preparation of the potassium salt which is more rapid than either of those described by Kehrmann (Abstr., 1887, 220) or Marshall (Trans., 1891, **59**, 760). When a solution of a cobalt salt is treated successively with glycerol, sodium hydroxide, and bromine water, and the mixture is boiled, a black solution is obtained of a *compound* which is probably



A solution of nickelic acetate can be obtained by dissolving freshly precipitated nickelic hydroxide in well-cooled 90 per cent. acetic acid. This solution gradually undergoes reduction in the cold, instantaneously on warming, and is immediately reduced by all reducing agents. Similar solutions can be obtained by the action of citric and tartaric acids on nickelic hydroxide. When freshly precipitated nickelic hydroxide is treated with a nearly saturated solution of potassium hydrogen sulphate, a solution is obtained which is a powerful oxidising agent and contains either a simple or complex nickelic sulphate. When cobaltic hydroxide is treated in this way, a cobaltic sulphate is not produced. E. G.

Ethyl Carbacetoacetate and Ethyl *iso*Dehydroacetate. FRANZ FEIST [with OTTO BEYER] (*Annalen*, 1906, **345**, 60—99).—It is still uncertain whether the ethyl carbacetoacetate prepared by Duisberg by the action of hydrogen chloride on ethyl acetoacetate is identical with the ethyl *iso*dehydroacetate prepared by Hantzsch by the action of concentrated sulphuric acid on ethyl acetoacetate. Genvresse believed that he had shown that the two esters were distinct, whilst Hantzsch and Polonowska maintained that they were identical. It is, however, found that they are identical, the so-called ethyl carbacetoacetate being only an impure ethyl *iso*dehydroacetate.

Ethyl *iso*dehydroacetate (ethyl carbacetoacetate) was prepared by Duisberg and Genvresse's methods, but did not give correct analytical numbers until it had been fractionated several times; it melts at 15° and distils without decomposition at 177° under 16 mm. pressure, and when pure gives no coloration with ferric chloride (compare Genvresse). Its molecular weight was determined by Beckmann's method in ether.

The monobromo-derivative of ethyl carbacetoacetate described by Genvresse was found not to exist, the ethyl bromo*iso*dehydroacetate, which melts at 87°, being alone obtained; it crystallises in the monoclinic system [$a : b : c = 0{\cdot}5891 : 1 : 0{\cdot}32796$; $\beta = 95°22'$]. When hydrolysed with aqueous potash, methyl trimethenyldicarboxylic acid (m. p. 200°), which was obtained by Genvresse, was alone produced.

Ethyl chloro*iso*dehydroacetate was also prepared by Genvresse's method; although identical in properties (m. p. 57—58°) with Genvresse's ethyl chlorocarbacetoacetate, the analyses showed that it was a derivative of the *iso*dehydroacetate.

The products of hydrolysis of the *iso*dehydroacetate by barium or sodium hydroxide were identical with those obtained by Genvresse by the use of the former base, a mixture of *cis*- and *trans*-β-methylglutaconic acids being formed. Hantzsch and Anschütz, who had used only a very concentrated solution of a base instead of the $2N$ NaOH solution used here, only observed the formation of the trans-acid.

The hydrolysis is effected by boiling the ester with 3—4 molecules of sodium hydroxide ($2N$) for eight to ten minutes; the yield of the *cis*-acid is increased by use of the smaller amount of base. The two acids are separated by successive fractional extraction of the mixture with ether, chloroform, and water. *trans*-β-Methylglutaconic acid can also be prepared by the addition of ethyl sodiomalonate to ethyl tetrolate; the ester thus obtained is purified by fractionation and boils at 260—270°. It is converted into the β-methylglutaconic acid by hydrolysis with sodium hydroxide, and melts at 115—116°, the melting point of Genvresse's compound. The *calcium* salt prepared from both acids crystallises with $4H_2O$ and the barium salt with 2—$3\frac{1}{2}H_2O$, but not with $6H_2O$, as stated by Genvresse; the *silver* salt, $2C_6H_6O_4Ag_2,AgOH,H_2O$, was also prepared. This acid combines with bromine but slowly, the product yielding when hydrolysed methyltrimethenyldicarboxylic acid. With hydrogen bromide, bromo-β-methylglutaric acid is obtained, melting at 129°. *Ethyl αβ-dibromo-β-methylglutarate*, $CO_2Et{\cdot}CH_2{\cdot}CBrMe{\cdot}CHBr{\cdot}CO_2Et$, is obtained by the combination of bromine with ethyl β-methylglutaconate and is an oil which cannot be distilled. When hydrolysed with alkali hydroxides, it behaves in two different ways, according to the quantity of base used. With excess of potassium hydroxide, *trans*-β-methylglutaconic acid together with a small quantity of the *cis*-form is produced. With the calculated quantity of base, *ethyl α-hydroxy-β-methylglutaconate*, $CO_2Et{\cdot}CH{:}CMe{\cdot}CH(OH){\cdot}CO_2Et$, which is an oil boiling at 265—270°, is formed; in the latter case, hydrogen bromide is eliminated and the second bromine atom replaced by a hydroxyl group. It is noted that in the action of potassium hydroxide on the dibrominated ester, methyltrimethenyldicarboxylic acid is not formed.

cis-β-Methylglutaconic acid, obtained both by the action of an alkali hydroxide on ethyl *iso*dehydroacetate and on the so-called ethyl carbacetoacetate, is shown to be identical both with Hantzsch's "homomesaconic" acid and with Genvresse's acid; the correct melting point is 146·5°, whilst Hantzsch records 147° and Genvresse 141°. The latter fact, together with some other reactions, led Genvresse to regard his acid as distinct from Hantzsch's. The *calcium* salt, $C_6H_6O_4Ca,4H_2O$, is crystalline, the *barium* salt crystallises in leaflets with $5H_2O$, and the copper salt (with $2H_2O$) is a pale bluish-green precipitate.

The acid obtained by Anschütz, Bendix, and Kerp by the action of excess of highly concentrated alkali hydroxide on ethyl *iso*dehydroacetate has been investigated; their observations have been confirmed; two acids are formed: one in very small quantity, melting at 149°, and a second, which is always present in a much greater proportion, melts at 234° (Anschütz, 228°). Alteration of the concentration of the alkali hydroxide within certain limits only changes to a small extent the proportion of the two acids. Analyses and molecular weight determinations show the formula of the acid melting at 234° to be $C_{15}H_{18}O_6Me_3$. K. J. P. O.

β-Methylglutaconic Acid and $a\beta$-Dimethylglutaconic Acid. FRANZ FEIST and OTTO BEYER (*Annalen*, 1906, **345**, 117—126).—The two β-methylglutaconic acids, which have been obtained both by Genvresse and the authors from ethyl *iso*dehydroacetate (preceding abstract), show that Thorpe (Trans., 1905, **87**, 1669) was in error in concluding that only the *trans*-β-methylglutaconic acid (m. p. 149°) is capable of existence. His view, therefore, as to the influence of a methyl group on the stereoisomerism shown by these acids is no longer supported by the experimental evidence.

It is found, however, that the presence of this methyl group greatly reduces the reactivity of the neighbouring CH group.

In order to demonstrate with greater certainty the constitution of β-methylglutaconic acid, it was reduced by hydriodic acid and red phosphorus to β-methylglutaric acid (m. p. 85—86°). Ethyl β-methylglutaconate was converted into ethyl $a\beta$-dimethylglutaconate by heating with methyl iodide and sodium in the presence of a small quantity of alcohol at 120° under pressure. The $a\beta$-dimethyldiglutaconic acid obtained by hydrolysis of this ester had all the properties ascribed to it by Thorpe (*loc. cit.*) and melted at 145°.

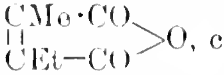
Ethyl β-methylglutaconate readily condenses with benzaldehyde, yielding when hydrolysed *a-benzylidene-β-methylglutaconic acid*, melting and decomposing at 169°. With diazonium salts, nitrous acid, and nitrosodimethylaniline, the ester reacts but slowly. K. J. P. O.

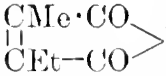
Antimony Tartrate. J. BOUGAULT (*Compt. rend.*, 1906, **142**, 585—586).—The product $SbC_4H_5O_7$, prepared by Guntz's process (Abstr., 1887, 657), is a mixture of antimony tartrate with an ethyl ether of antimony tartrate. If the alcohol used in this process is replaced by acetone, the *antimony tartrate* obtained has the composition $SbC_4H_3O_6$, that is, it contains a mol. of water less than Guntz's product, due probably to an internal esterification between a carboxyl and a hydroxyl group of the acid. It crystallises in small lamellæ, dissolves in 125 parts of water, and is dissociated when diffused in a quantity of water insufficient to dissolve it. The salt gives all the reactions of "tartar emetic," which may be prepared from it by solution in the necessary quantity of an aqueous solution of potassium hydrogen carbonate. Its solubility in aqueous solutions of potassium acetate and potassium hydrogen carbonate serve to distinguish it from antimony ethyl tartrate. T. A. H.

Constitution of Hæmatic Acid. WILLIAM KÜSTER [with H. GALLER, K HAAS and OTTO MEZGER] (*Annalen*, 1906, **345**, 1—59. Compare Abstr., 1901, i, 58, 298).—The constitution of the hæmatic acids, $C_8H_8O_5$ and $C_8H_9O_4N$, previously suggested (Abstr., 1902, i, 845), which denotes them as the anhydride and imide respectively of the acid Δγ-pentene-αγδ-tricarboxylic acid,

$$CO_2H\cdot CMe\colon C(CO_2H)\cdot CH_2\cdot CH_2\cdot CO_2H,$$

has been confirmed by a series of detailed experiments.

Methylethylmaleic anhydride,  $\begin{array}{l}\mathrm{CMe\cdot CO}\\ \Vert\\ \mathrm{CEt-CO}\end{array}\!\!>\mathrm{O}$, could not be prepared by the condensation of methylsuccinic acid and pyruvic acid in the presence of acetic anhydride, but was obtained from methyl ethylacetoacetate; the latter was condensed with hydrogen cyanide in ethereal solution, and the product of the reaction immediately hydrolysed with hydrochloric acid; the anhydride, which was purified by means of the *barium* salt, $C_7H_8O_4Ba,H_2O$, is an oil boiling at 229·7—230·7° (corr.) under 760 mm. pressure; it has a sp. gr. 1·31 at 15° and $K = 0·0094$ at 25°. It forms insoluble zinc, ferrous, and copper salts. Its *silver* salt is an amorphous precipitate. *Methyl methylethylmaleate*, prepared from the silver salt and methyl iodide, is a colourless liquid boiling at 235°. With ammonia in ethereal solution, the anhydride yields the *ammonium* salt of a monoamide, $NH_2\cdot CO\cdot CMe\colon CEt\cdot CO_2\cdot NH_4$, which is a crystalline solid, soluble in water.

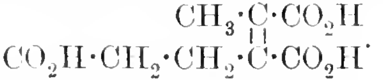
The *imide* of methylethylmaleic acid,  $\begin{array}{l}\mathrm{CMe\cdot CO}\\ \Vert\\ \mathrm{CEt-CO}\end{array}\!\!>\mathrm{NH}$, is obtained by heating the anhydride with alcoholic ammonia under pressure at 130°, and forms colourless crystals melting at 66—67°. This imide is identical with the substance obtained by heating the hæmatic acid, $C_8H_9O_4N$, with alcoholic ammonia at 130°, and yields, on hydrolysis with barium hydroxide, a salt from which methylethylmaleic anhydride can be obtained; the *calcium* salt, $C_7H_8O_4Ca,H_2O$, prepared from the anhydride from the latter source, crystallises in leaflets.

The hæmatic acid, $C_8H_9O_4N$, begins to decompose at 230°, carbon dioxide being evolved and the imide of methylethylmaleic acid formed. When the other hæmatic acid, $C_8H_8O_5$, is heated at 150°, carbon dioxide is evolved and methylethylmaleic anhydride formed.

On oxidising hæmatic acid, $C_8H_8O_5$, with potassium permanganate, succinic acid was alone produced; chromic acid in acetic acid solution also yields succinic acid, the pyruvic acid, which was expected, probably being further oxidised.

On reducing this hæmatic acid, $C_8H_8O_5$, with hydriodic acid, a tribasic acid, *hæmotricarboxylic acid*, $C_5H_9(CO_2H)_3$, can be isolated, which melts at 145°; its *silver* salt is an amorphous precipitate, and its *copper* salt a bluish-green precipitate; the *cadmium* salt, $(C_8H_9O_6)_2Cd_3,2H_2O$, is a white powder, and the *calcium* salt (with H_2O) a gummy mass. The tribasic acid was also obtained together with an isomeride by reducing the same hæmatic acid by zinc dust and acetic acid, after attempts with sodium and amyl alcohol and sodium amalgam in acid solution had failed; the product of the reduction was separated into two fractions by crystallisation from water; the one, hæmotricarboxylic acid, melting at 140—141°, forms two-thirds of the reduction product; it crystallises in rosettes of needles and has $K = 0{\cdot}02108$, and the barium and calcium salts crystallise each with H_2O, properties which show it to be identical with the hæmotricarboxylic acid (m. p. 145°) obtained by reduction with hydriodic acid; the *methyl* ester was prepared from the silver salt and is a yellow oil boiling at 293°. All attempts to obtain an anhydride from this tricarboxylic acid failed.

The less fusible isomeride, the hæmotricarboxylic acid melting at 175—176°, crystallises in needles and has $K = 0{\cdot}2274$; its *barium* salt, $(C_8H_9O_6)_2Ba_3,H_2O$, and its other salts resemble those of the isomeride (m. p. 140°). Attempts to prepare an anhydride led to the complete conversion of the acid into the isomeride. This isomeric change is also effected by heating the acid (with the higher melting point) with water or hydrochloric acid under pressure at 200°. The reverse change could not be brought about. This behaviour is in agreement with the view that the pentenetricarboxylic acid is a derivative of maleic acid, thus:



$$\begin{array}{c} CH_3\cdot C\cdot CO_2H \\ \| \\ CO_2H\cdot CH_2\cdot CH_2\cdot C\cdot CO_2H \end{array}.$$

In the reduction, two asymmetric carbon atoms are produced, and thus two inactive hæmotricarboxylic acids exist.

The reduction of the hæmatic acid, $C_8H_9O_4N$, by hydrogen iodide and phosphonium iodide seems to lead only to the production of a mixture of the two stereoisomeric hæmotricarboxylic acids. When zinc dust and acetic acid were used, no definite results were obtained, partial hydrolysis of the imide, as well as reduction, having taken place. An impure *imide*, $C_8H_{11}O_4N$, was obtained and melted at 80—83°; the calcium salt, $(C_8H_{10}O_4N)_2Ca,2H_2O$, was analysed. When hydrolysed with 50 per cent. sulphuric acid, a mixture of the two isomeric hæmotricarboxylic acids was obtained.

Attempts were made to reduce methylethylmaleic anhydride, using in the first place hydriodic acid and then zinc dust and acetic acid, aluminium amalgam in sulphuric acid solution, and finally sodium amalgam in alkaline solution. In all cases except the last, a small yield of the fumaroid form of methylethylsuccinic acid (m. p. 172—173°) was obtained.

K. J. P. O.

Constitution of Platinum Bases. SOFUS M. JÖRGENSEN (*Zeit. anorg. Chem.*, 1906, **48**, 374—388. Compare Abstr., 1900, i, 542; 1901, i, 163).—When the ethylenediamine salt of Zeise's acid is treated with several times its weight of cold water, hydrogen chloride is eliminated and a new compound, s-*platoethylenediamine-ethylene chloride*, separates in very small, yellow crystals according to the equation:

$$C_2H_4N_2H_6(Cl_2PtC_2H_4Cl)_2 = C_2H_4(ClNH_2PtC_2H_4Cl)_2 + 2HCl;$$

the reaction is a reversible one. Two other methods for the preparation of this compound are given. When, on the other hand, the ethylenediamine salt of Zeise's acid is heated in aqueous solution, a substance, already described by Griess and Martius (*Annalen*, 1861, **120**, 225), separates in yellow needles; the author shows that this compound is s-*platoethylenediamine chloride*, $C_2H_4(ClNH_2)_2Pt$, previously obtained by him by other methods (*loc. cit.*).

The second part of the paper deals with the question as to which of the two formulæ, $ClNH_3PtNH_3Cl$ and $ClPtNH_3NH_3Cl$, pertains to the chloride first described by Peyrone, and which to Reiset's so-called second chloride. The author, in a former paper, has contended that, contrary to the view of Cleve and Blomstrand, the symmetrical constitution is to be ascribed to Peyrone's chloride and considers that he has now decided the question in his favour by showing that the compound of Peyrone's chloride with dimethylamine is isomeric and not identical with the compound which ammonia forms with the dimethylamine compound corresponding with Peyrone's chloride; only the chloride with a symmetrical constitution can give isomerides in these circumstances.

Dimethylamine platinochloride, $Pt[(CH_3)_2NH]_2Cl_2$, already described by Koefoed, was obtained by interaction of potassium platinochloride and dimethylamine in aqueous solution, and occurs in rhombic plates. The structure of this compound is similar to that of Peyrone's salt, since the pyridine compound corresponding with the latter gives the same compound with dimethylamine as Koefoed's salt by interaction with pyridine in aqueous solution. Further, the mixed dimethylamine ammonia salts, obtained by interaction of Peyrone's salt with dimethylamine and of Koefoed's salt with ammonia, although distinct (see later), yield the same products when heated with hydrochloric acid. Koefoed's salt dissolves slowly in cold aqueous dimethylamine, and from the solution a compound was isolated which with ammonia yielded a platodiammine different from that obtained by the action of ammonia on Koefoed's salt, but identical with the salt obtained by the action of dimethylamine on Reiset's chloride, a further proof that Koefoed's salt corresponds in constitution with Peyrone's salt.

The mixed *platodiammine* salt, $Pt\{(NH_3)_2[(CH_3)_2NH]_2\}Cl_2$, obtained by the action of ammonia on Koefoed's salt, forms colourless, crystalline masses; the isomeric compound obtained by interaction of Peyrone's chloride and dimethylamine forms large, clear plates. As these compounds readily change the one into the other, their double salts with platinous chloride, obtained by interaction of the respective compounds with potassium platinochloride in acidified aqueous solution, have been investigated. The double salt obtained from the compound first mentioned occurs in light yellow, anhydrous needles, which are not dichroic; the isomeric salt forms red dichroic needles which crystallise with $1H_2O$. It is shown by solubility determinations at the ordinary temperature that these double salts are distinct substances.

G. S.

The Precipitability of Amino-acids by Phosphotungstic Acid. PHOEBUS A. LEVENE and W. BEATTY (*Zeit. physiol. Chem.*, 1906, **47**, 149—150).—As a rule, amino-acids are precipitable only from concentrated solutions by a concentrated solution of phosphotungstic acid. Particulars in relation to the following amino-acids are given: glycine, alanine, leucine, phenylalanine, and glutamic acid.

W. D. H.

Amine Derivatives of Mesoxalic Esters. RICHARD S. CURTISS (*Amer. Chem. J.*, 1906, **35**, 354—358).—*Ethyl dihydroxyiminodi-*

malonate, $NH[C(OH)(CO_2Et)_2]_2$, prepared by the action of dry ammonia on a well-cooled solution of ethyl dihydroxymalonate in benzene in presence of zinc chloride, crystallises from ether in flat, rectangular tablets, melts at 103—105°, decomposes at 105—110° with evolution of ammonia, is soluble in benzene, ethyl acetate, acetone, or chloroform, and is rapidly decomposed by water. This compound can also be obtained by the action of ammonia on ethyl oxomalonate. E. G.

Derivatives of Formhydroxamic Acid and the Possible Existence of Esters of Fulminic Acid. II. HENRY C. BIDDLE (*Amer. Chem. J.*, 1906, **35**, 346—353).—In an earlier paper (Abstr., 1905, i, 181), it was shown that when methyl chloroformoxime is treated with potassium hydroxide, a compound is produced which, it was suggested, might be methyl fulminate. A further study of the reaction has proved that the substance is not methyl fulminate, but is methyl di-imino-oxalate which has been synthesised by the following method.

By the action of chlorine on a solution of potassium cyanide in methyl alcohol diluted with water, a mixture of methyl cyanoiminocarbonate and methyl di-imino-oxalate is produced. *Methyl cyanoiminocarbonate*, $NH{:}C(OMe){\cdot}CN$, is a colourless, mobile liquid, which boils at 33—34° under 22 mm. pressure, has a peculiar, *iso*nitrile-like odour, is slightly soluble in water, and is somewhat unstable. *Methyl di-imino-oxalate*, $NH{:}C(OMe){\cdot}C(OMe){:}NH$, crystallises in colourless, transparent plates, has a peculiar, sweet odour, and is more stable than methyl cyanoiminocarbonate, although it gradually changes into a dark resin. When the ester is treated with dilute hydrochloric acid, it is converted into ammonia and methyl oxalate. E. G.

Preparation of Acetamide. MAURICE FRANÇOIS (*J. Pharm. Chim.*, 1906, [vi], **23**, 230—237).—When ammonium acetate is heated, it decomposes, producing ammonia and ammonium hydrogen acetate; the latter on further heating yields water, acetic acid, and acetamide. The ordinary laboratory process of preparing acetamide by distilling ammonium acetate therefore gives a poor yield not exceeding 28 per cent. of the theoretical. By starting with ammonium hydrogen acetate, a yield of acetamide equivalent to 45·3 per cent. of the theoretical can be obtained. The special apparatus employed by the author in distilling the diacetate is figured in the original.

T. A. H.

Dialkylmalonamides. KARL BÖTTCHER (*Chem. Zeit.*, 1906, **25**, 272).—In opposition to Meyer (this vol., i, 138), the author finds that methylethylmalonyl chloride reacts with concentrated aqueous ammonia to give a 90 per cent. yield of the corresponding diamide, and not methylethylacetamide, as stated by Meyer. P. H.

Mercuric Oxycyanide. ERWIN RUPP (*Arch. Pharm.*, 1906, **244**, 1—2).—The abnormal character of mercuric oxycyanide, $Hg(CN)_2,HgO$, may be explained by regarding it as a complex salt with the ions $\cdot Hg\cdot O\cdot Hg\cdot$ and $2\cdot CN$. C. F. B.

Hydrargyrum Oxycyanatum. VON PIEVERLING (*Arch. Pharm.*, 1906, **244**, 35—36).—The pastilles of this substance no longer contain sodium chloride.

Mercuric oxycyanide does not equal the cyanide in its power of killing bacteria; it is its power of preventing their development which is remarkable. C. F. B.

Arsonic and Arsinic Acids. WILLIAM M. DEHN and S. J. MCGRATH (*J. Amer. Chem. Soc.*, 1906, **28**, 347—361).—The arsonic and arsinic acids are white, crystalline substances which are soluble in water or alcohol, but insoluble in ether.

Magnesium n-*propylarsonate*, $MgAsPr^{a}O_3$, prepared in the same manner as the ethylarsonate (Abstr., 1905, i, 184), forms pearly-white, soapy crystals containing $\frac{1}{2}H_2O$. When this salt is treated with the calculated quantity of strong sulphuric acid and the product is extracted with alcohol, n-*propylarsonic acid*, $AsPr^{a}O(OH)_2$, is obtained, which crystallises in needles and melts at 125°; an aqueous solution, saturated at 26°, contains 43 per cent. of the acid. When a solution of the magnesium salt in dilute hydrochloric acid is treated with hydrogen sulphide, n-*propylarsine disulphide*, $Pr^{a}AsS_2$, is obtained as a light yellow, viscid oil which has a sp. gr. 1·8 and, when cooled below −10°, becomes a gummy mass.

iso*Amylarsonic acid*, $C_5H_{11}\cdot AsO(OH)_2$, forms pearly-white crystals, melts at 194°, is soluble in water at 28° to the extent of 0·82 gram in 100 c.c. and in alcohol at 21° to the extent of 2·2 grams in 100 c.c. iso*Amylarsine disulphide*, $C_5H_{11}\cdot AsS_2$, is a viscid, light yellow oil, which cannot be distilled without decomposition.

Benzylarsonic acid, $CH_2Ph\cdot AsO(OH)_2$, crystallises in long, white, lustrous needles, has a bitter taste, melts at 167°, and is stable in the air; 100 c.c. of an aqueous solution, saturated at 22·5°, contain 0·34 gram; at 27°, 0·39 gram; and at 97°, 3·50 grams of the acid; a saturated alcoholic solution at 23° contains 0·87 gram, and at 70°, 5·91 grams of the acid in 100 c.c. *Benzylarsine disulphide* is a heavy, bright yellow oil which, on heating, decomposes with evolution of hydrogen sulphide and formation of arsenious oxide and stilbene. When benzylarsonic acid is heated, it undergoes decomposition with production of benzyl alcohol, benzaldehyde, stilbene, arsenious oxide, and water. The acid is decomposed by concentrated hydrochloric acid with formation of benzyl chloride and arsenious acid, and more rapidly by sulphuric acid with formation of dibenzyl, benzaldehyde, and arsenious acid.

Magnesium ethylarsonate is decomposed by heat into magnesium oxide, metallic arsenic, methane, ethylene, and water. When magnesium *n*-propylarsonate is heated, it yields a gaseous mixture consisting of hydrogen, methane, ethylene, and propylene.

Determinations have been made of the rate of transformation of potassium arsenite into arsonic acids at 25° when treated with *iso*butyl iodide, chloroform, bromoform, iodoform, *p*-chlorotoluene, and allyl iodide; the results are tabulated.

The following solubilities have been determined, the quantity in each case being the number of grams of the substance contained in

100 c.c. of the solution saturated at the given temperature. Ethylarsonic acid in water at 27°, 70·00; at 40°, 112·00; and in alcohol at 25°, 39·40. Phenylarsonic acid in water at 28°, 3·25; at 41°, 4·82; at 52°, 8·52; and at 84°, 24·0; in alcohol at 26°, 15·51, and at 68°, 55·40. Methylarsinic acid in water at 22°, 82·90. Phenylarsinic acid in water at 27°, 0·28; in alcohol at 22°, 11·80, and at 55°, 57·70.

Ethylarsonic acid melts at 99·5°, phenylarsonic acid at 158·0°, and phenylarsinic acid at 164·0°. E. G.

Siliconium, Boronium, and Titanonium Salts. Walther Dilthey [and, in part, F. Eduardoff and F. J. Schumacher] (*Annalen*, 1906, **344**, 300—342. Compare Abstr., 1903, i, 405, 591; 1904, i, 132, 290; Dilthey and Eduardoff, Abstr., 1904, i, 464; this vol., i, 128; Werner, Abstr., 1902, ii, 554; Baeyer, Abstr., 1905, i, 281).—Siliconium, boronium, and titanonium chlorides are formed by the action of silicon tetrachloride, boron trichloride, and titanium tetrachloride respectively on $\alpha\gamma$-diketones. The chlorides can be converted into bromides, iodides, periodides, nitrates, and sulphates, and yield additive compounds with metallic salts. In these "onium" salts, the metalloid atom must be attached to oxygen, the derivatives of acetylacetone, for example, having the constitutions

$$Si(O\cdot CMe{:}CHAc)_3Cl,$$

$Ti(O\cdot CMe{:}CHAc)_3Cl$, and $B(O\cdot CMe{:}CHAc)_2Cl$, respectively, as they are formed the more easily the more stable is the enolic form of the diketone, and are readily hydrolysed by water or moist air, whilst compounds such as triphenylsilicon chloride and phenylboron dichloride, in which the metalloid atom is attached directly to carbon, are stable towards water. The siliconium salts resemble trimethoxysilicon chloride, $Si(OMe)_3Cl$, but whilst the chlorine atom of the latter can be substituted by alkyl groups, the chlorine atom of the siliconium chlorides cannot be substituted by alkyl groups or by diketones, and the compound has the character of a salt. This difference in the function of the chlorine atom is explained by means of Werner's co-ordination theory.

Triacetylacetonylsiliconium zincochloride, $Si(O\cdot CMe{:}CHAc)_3ZnCl_3$, forms white needles and becomes brown at about 240°, but does not melt at 300°. The *iodide*, $Si(O\cdot CMe{:}CHAc)_3I$, formed by the action of hydrogen iodide on the chloride in glacial acetic acid solution, crystallises in glistening, white needles; the *periodide*, $Si(O\cdot CMe{:}CHAc)_3I_3$, crystallises in violet needles; the *picrate* forms yellow needles and decomposes slowly on exposure to air.

Triacetylmethylacetonylsiliconium ferrichloride,

$$Si(O\cdot CMe{:}CMeAc)_3FeCl_4,$$

forms long, pointed, greenish-yellow leaflets and melts at 210°; the unstable *aurichloride*, $Si(O\cdot CMe{:}CMeAc)_3AuCl_4$, crystallises in slender, golden-yellow needles and melts and decomposes at 206°; the *platinichloride*, $[Si(O\cdot CMe{:}CMeAc)_3]_2PtCl_6$, forms yellow needles and commences to blacken at 280°; the white, crystalline *zincochloride*,

$$Si(O\cdot CMe{:}CMeAc)_3ZnCl_3,$$

melts at 220°. *Triacetylethylacetonylsiliconium ferrichloride*,

$$Si(O\cdot CMe{:}CEtAc)_3FeCl_4,$$

crystallises in yellow needles and melts at 157°; the *aurichloride*, $Si(O\cdot CMe{:}CEtAc)_3AuCl_4$, forms golden-yellow needles and melts at

148°; the *platinichloride*, $[Si(O\cdot CMe:CEtAc)_3]_2PtCl_6$, crystallises in orange prisms, and decomposes but does not melt below 300°; the *periodide*, $Si(O\cdot CMe:CEtAc)_3I_3$, crystallises in violet prisms.

The *tribenzoylacetonylsiliconium platinichlorides* formed from the isomeric ferrichlorides are obtained as long, slender, yellow needles and nodular aggregates of orange-yellow crystals respectively; the two preparations are equally insoluble, and decompose without melting at about 200°.

Tridibenzoylmethylsiliconium zincochloride, $[Si(O\cdot CPh:CHBz)_3]_2ZnCl_4$, formed by the action of zinc chloride on tridibenzoylmethylsiliconium chloride in glacial acetic acid solution, crystallises in sheaves of white needles and is only slowly decomposed by aqueous sodium carbonate. The action of stannic chloride ($\frac{1}{2}$ mol.) on the chloride in chloroform solution leads to the formation of the *stannichloride*,

$$[Si(O\cdot CPh:CHBz)_3]_2SnCl_6,$$

which separates in stout crystals, is insoluble in most solvents, but dissolves in ethylene dibromide and melts above 305°, at which temperature it is only slightly decomposed. It dissolves in a chloroform solution of stannic chloride, from which, on addition of glacial acetic acid, the *stannichloride*, $Si(O\cdot CPh:CHBz)_3SnCl_5$, separates in yellow needles; this melts when quickly heated at 290—291°, is readily soluble in chloroform, and when left in contact with a mixture of chloroform and glacial acetic acid is reconverted into the normal stannichloride. The *compound* with antimony pentachloride,

$$Si(O\cdot CPh:CHBz)_3SbCl_6,$$

separates from glacial acetic acid in yellow crystals and is readily soluble in chloroform.

The compound of silicon tetrachloride with ethyl acetoacetate (Rosenheim, Loewenstamm, and Singer, Abstr., 1903, i, 603) is much less stable than triacetylacetonylsiliconium chloride, as it is decomposed by ferric chloride in glacial acetic acid solution. The crystalline *ferrichloride*, $Si(O\cdot CMe:CH\cdot CO_2Et)_3FeCl_4$, formed in chloroform solution, is unstable. Ethyl benzoylacetate reacts with silicon tetrachloride only with difficulty, whilst ethyl malonate does not form siliconium salts.

In the absence of a solvent, silicochloroform and acetylacetone interact with explosive violence, but in the presence of much chloroform the interaction leads to the formation of triacetylacetonylsiliconium chloride hydrochloride, hydrogen chloride, and hydrogen; the same siliconium compound is formed by the interaction of phenylsilicon trichloride and acetylacetone.

The methods of preparation, the properties, and the reactions of the boronium salts are similar to those of the siliconium salts, the two groups differing chiefly in their stability. The *compound* formed by the action of acetylacetone on boron trichloride in ethereal solution, $B(CO\cdot CMe:HAc)_2Cl$ or $B(O\cdot CMe:CHAc)_2Cl,HCl$, is extremely unstable. The *ferrichloride*, BR_2FeCl_4, crystallises in lemon-yellow leaflets and melts and decomposes at 137°; the *aurichloride*, BR_2AuCl_4, crystallises from a mixture of chloroform and ether in leaflets and melts at 135°; the *platinichloride*, $(BR_2)_2PtCl_6$, forms large, reddish-yellow crystals and blackens at about 180°, but does not melt at 300°; the *iodide*, BR_2I, forms unstable, yellow crystals; the *periodide*

BR_2I_3, separates in glistening, stout, reddish-brown crystals; the crystalline *sulphate* is deliquescent; the *zincochloride*, BR_2ZnCl_3, forms coarse, white crystals and melts and decomposes at 206°; the *stannichloride*, BR_2SnCl_6, crystallises in slender, white prisms and melts at 210—212°.

The *compound* of boron trichloride with benzoylacetone,

$$B(CHAcBz)_2Cl\ [?\ B(O{\cdot}CMe{:}CHBz)_2Cl],$$

or its *hydrochloride* is obtained as an unstable, yellowish-white substance which is readily soluble in glacial acetic acid or chloroform. The *ferrichloride*, $B(CHAcBz)_2FeCl_4$, forms nodular aggregates of stout, yellow crystals and slender, yellow needles, the latter form only being obtained on recrystallisation of the salt from chloroform; it melts at 180—182°; the *platinichloride* is stable and insoluble; the *zincochloride*, $B(CHAcBz)_2ZnCl_3$, is obtained in stout plates melting at 208° and in long needles melting at about 220°; when recrystallised from hot glacial acetic acid, both forms yield colourless needles melting at 223—225°; the *iodide*, $B(CHAcBz)_2I$, is obtained as a reddish-yellow powder, which appears under the microscope as a mixture of a yellow with a violet-brown substance, and on recrystallisation from chloroform forms yellow crystals melting at 210°; the *periodide*, $B(CHAcBz)_2I_3$, forms violet-brown, glistening prisms with green lustre; the *stannichloride*, $[B(CHAcBz)_2]_2SnCl_6$, was analysed.

The action of boron trichloride on dibenzoylmethane in ethereal solution leads to the formation of an extremely unstable, white, crystalline product which loses hydrogen chloride when dried.

Titanium tetrachloride and acetylmethylacetone interact in glacial acetic acid solution, forming the *compound* $[Ti(O{\cdot}CMe{:}CMeAc)_3]_2,TiCl_6$, which separates in yellowish-red crystals and decomposes slowly on exposure to moist air. The *ferrichloride*, $Ti(O{\cdot}CMe{:}CMeAc)_3FeCl_4$, formed by the action of titanium tetrachloride on a glacial acetic acid solution of acetylmethylacetone and anhydrous ferric chloride, is obtained as a brownish-red, crystalline product, soluble in ethyl acetate or hot glacial acetic acid.

The red *product*, $[Ti(CHAcBz)_3]_2TiCl_6$, formed by the interaction of titanium tetrachloride and benzoylacetone, is only moderately stable.

The unstable, dark red, crystalline *product*, $[Ti(O{\cdot}CPh{:}CHBz)_3]_2,TiCl_6$, was analysed.

Salicylaldehyde interacts with titanium tetrachloride in the same manner as the $\alpha\gamma$-diketones, forming an unstable titanonium salt. The *product* of the interaction of ethyl salicylate and titanium tetrachloride crystallises in yellowish-red needles and deliquesces immediately on exposure to air. *o*-Hydroxyacetophenone and *o*-hydroxybenzophenone yield similar red, unstable *titanonium* salts.

Stannic chloride interacts with acetylacetone or its copper derivative in chloroform solution, forming the *product* $Sn(O{\cdot}CMe{:}CHAc)_2Cl_2$, which melts at 203° and is decomposed by ferric chloride or hydrogen iodide, yielding in the latter case stannic iodide. Stannic bromide interacts with $\alpha\gamma$-diketones in the same manner as the chloride.

The product of the interaction of antimony pentachloride and acetylacetone (compare Rosenheim, Loewenstamm, and Singer, *loc. cit.*) has the molecular formula $Sb(O{\cdot}CMe{:}CHAc)Cl_4$, crystallises in yellow plates or leaflets, melts at 137°, and is decomposed by ferric chloride or hydrogen iodide. Antimony pentachloride interacts with other diketones such as dibenzoylmethane to form yellow substitution products.

G. Y.

Nitration of *o*- and *m*-Dibromobenzenes. ARNOLD F. HOLLEMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, **8**. 678—680. Compare Abstr., 1905. i, 41, 42).—*m*-Dibromobenzene, prepared from pure *m*-bromoaniline, solidifies at −7° and has the sp. gr. 1·960 at 18·5°. *o*-Dibromobenzene, prepared from *o*-bromoaniline, solidifies at 6° and has the sp. gr. 1·996 at 11°. The six dibromonitrobenzenes have been prepared in the same way as the dichloronitrobenzenes (*loc. cit.*). The composition of the products of nitration at 0° were determined from their solidifying points and their sp. gr. Whilst *o*-dichlorobenzene yields 7·2 per cent., and *m*-dichlorobenzene 4·0 per cent., *o*-dibromobenzene yields 18·3 per cent., and *m*-dibromobenzene 4·6 per cent. of the by-product.

G. Y.

Introduction of Halogen Atoms into the Benzene Nucleus during the Reduction of Aromatic Nitro-compounds. JAN J. BLANKSMA (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, **8**, 680—683. Compare Abstr., 1905, i, 761; Goldschmidt and Ingebrechtsen, Abstr., 1904, ii, 608).—If 10 c.c. of nitrobenzene are boiled with 100 c.c. of alcohol and 200 c.c. of 25 per cent. hydrochloric acid in a reflux apparatus, and 15 grams of tin are added gradually in small portions, the reduction product consists of 55 per cent. of *o*- and *p*-chloroanilines, together with 45 per cent. of aniline. If the nitrobenzene is reduced slowly with stannous chloride and hydrochloric acid, 53 per cent. of the product consists of *o*- and *p*-chloroanilines. Similar results are obtained with nitrobenzene.

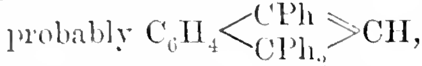
The slow reduction of nitrobenzene with tin and hydrobromic acid leads to the formation of a mixture of aniline and *o*- and *p*-bromoanilines.

The formation of the *o*- and *p*-chloro- and bromo-anilines must be in consequence of the intermediate production of phenylhydroxylamine.

G. Y.

New Aromatic Hydrocarbons. DANIEL VORLÄNDER and CARL SIEBERT (*Ber.*, 1906, **39**, 1024—1035).—*Tetraphenylallene*, $CPh_2:C:CPh_2$, is obtained when dry barium diphenylacetate is distilled under a pressure of 15—20 mm., the distillate freed from oil, and the solid product crystallised from hot acetone. It forms colourless needles or prisms, melts at 164—165°, and dissolves readily in most organic solvents with the exception of cold alcohol and light petroleum. When moistened with concentrated sulphuric acid, it becomes deep violet-brown, and dissolves to a greenish-violet-brown solution, which gradually changes to orange; similar changes in colour are observed with solutions of hydrogen chloride or bromide in glacial acetic acid, and are due to the formation of a new hydrocarbon which melts at 135°. Tetraphenylallene forms unstable, dark-coloured additive compounds with halogen hydracids at low temperatures, but does not combine with picric acid. It does not react with a boiling 20 per cent.

solution of potassium hydroxide, sodium ethoxide, acetic anhydride, alcoholic ammonia, phenylhydrazine, or boiling aniline, and does not combine with ethyl sodiomalonate or magnesium phenyl bromide. When reduced with red phosphorus and hydriodic acid in acetic acid solution, or with sodium and boiling alcohol, it yields *s-tetraphenylpropane*, $C_{27}H_{24}$, which crystallises from alcohol in needles melting at 139°. Oxidation with chromic acid in acetic acid solution converts the unsaturated hydrocarbon into benzophenone. When the oxidation is less vigorous, a *product* melting at 195—197° is obtained.

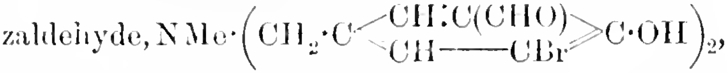
Tetraphenylallene is readily converted into an isomeric *hydrocarbon* $C_{27}H_{20}$, probably  $C_6H_4{<}\begin{smallmatrix}CPh\\CPh_2\end{smallmatrix}{>}CH$, when its acetic acid solution is saturated with hydrogen chloride, kept until it becomes colourless, and then poured into water. The hydrocarbon crystallises from methyl alcohol in colourless prisms, melts at 134—135°, is somewhat more readily soluble than its isomeride, and its solution in concentrated sulphuric acid has an orange-yellow colour. When brominated in chloroform solution, it yields a *monobromo*-derivative, $C_{27}H_{19}Br$, which crystallises from alcohol in flat needles melting at 167—168°. It is extremely stable, and the bromine is not removed by boiling with aqueous or alcoholic potassium hydroxide or by heating with lead oxide and acetic acid. It does not give a coloration with cold concentrated sulphuric acid, but when warmed an intense magenta-red coloration is developed. The same bromo-derivative is obtained by the action of bromine on tetraphenylallene.

When reduced, the new hydrocarbon yields a *product*, $C_{27}H_{22}$, melting at 113—114°, and, when oxidised, a neutral *product* melting at 146—148°.

Considerable quantities of diphenylmethane and small amounts of a *hydrocarbon* (mol. wt. about 320) which crystallises from aqueous alcohol in colourless needles melting at 121° are also formed when barium diphenylacetate is distilled. Hot hydrochloric acid transforms this hydrocarbon into an isomeride melting at 104°. Both compounds yield benzophenone when oxidised.

Tetraphenylallene has been synthesised by the following methods: A. *Tetraphenylpropylene*, $CHPh_2{\cdot}CH{:}CPh_2$, is readily formed when Kohler's $\alpha\alpha\gamma\gamma$-tetraphenylpropyl alcohol, diphenylethyldiphenylcarbinol (Abstr., 1904, i, 596), is boiled with acetic anhydride or 20 per cent. hydrochloric acid. It crystallises from alcohol in plates, melts at 127—128°, dissolves readily in benzene, chloroform, or acetone, and when reduced yields tetraphenylpropane. When suspended in chloroform and brominated, it yields *tetraphenylbromopropylene*, $C_{27}H_{21}Br$, melting at 124°, and this, with alcoholic potash, yields tetraphenylallene. B. [With J. OSTERBURG.] Kohler and Johnston's phenylbenzylideneacetophenone (Abstr., 1905, i, 215) reacts with an excess of magnesium phenyl bromide in ethereal solution, and the product, after treatment with dilute hydrochloric acid, yields *$\alpha\alpha\gamma\gamma$-tetraphenylpropylene alcohol*, $CPh_2{:}CH{\cdot}CPh_2{\cdot}OH$, which crystallises from alcohol in prisms melting at 138—139°. Its behaviour towards most reagents is similar to that of the allene derivative, and when boiled with acetic anhydride it is transformed into tetraphenylallene. J. J. S.

Molecular Compounds of Nitro-derivatives with Amines. Robert Kremann (*Ber.*, 1906, **39**, 1022—1024. Compare Noelting and Sommerhoff, this vol., i, 157).—The non-isolation of a definite additive compound cannot be regarded as direct evidence that the components cannot form such a compound. The only method for proving the non-existence of such compounds is the examination of the melting-point diagram as previously described (Abstr., 1905, ii, 76, 77). It is pointed out that meta- and para-disubstituted derivatives of benzene form additive compounds more readily than ortho derivatives. J. J. S.

Condensation Products of Organic Bases with ψ-Phenols containing Strongly Negative Substituting Groups. Karl Auwers and Otto Schröter (*Annalen*, 1906, **344**, 257—270. Compare this vol., i, 259).—The *methylamine* derivative of α-5-dibromo-6-hydroxy-3-methylbenzaldehyde,  $\mathrm{NMe\cdot\left(CH_2\cdot C{<}\begin{matrix}CH:C(CHO)\\ CH\text{———}CBr\end{matrix}{>}C\cdot OH\right)_2}$, formed by the action of aqueous methylamine on the ψ-phenol in concentrated benzene solution, is yellow, melts at 136—141°, is insoluble or only sparingly soluble in organic solvents, remains unchanged on prolonged heating on the water-bath, and is stable towards hot 5 per cent. aqueous sodium hydroxide or cold glacial acetic acid. When heated with glacial acetic acid, it is decomposed, forming the monoacetate of 5-bromo-α-6-dihydroxy-3-methylbenzaldehyde, melting at 102° (Auwers and Huber, Abstr., 1902, i, 213). When boiled with acetic anhydride the methylamine derivative yields the *diacetate*, $OAc\cdot C_6H_2Br(CHO)\cdot CH_2\cdot OAc$, which crystallises in stellate groups of needles and melts at 74—75°.

The *diethylamine* derivative, $NEt_2\cdot CH_2\cdot C_6H_2Br(CHO)\cdot OH$, crystallises from methyl alcohol in colourless plates and prisms and melts and becomes red at 146—147°, but when heated on the water-bath or boiled with 5 per cent. sodium hydroxide remains unchanged. When treated with cold glacial acetic acid, it is decomposed, yielding a small amount of a product, $CH_2[C_6H_2Br(CHO)\cdot OH]_2$ (?), which melts at about 187°. The diethylamine derivative yields the monoacetate melting at 102° when boiled with glacial acetic acid, and a non-nitrogenous *product* when boiled with acetic anhydride. The *diamylamine* derivative, $N(C_5H_{11})_2\cdot CH_2\cdot C_6H_2Br(CHO)\cdot OH$, crystallises in colourless leaflets, melts at 72—74°, is readily soluble in chloroform, benzene, or acetone, and decomposes extremely slowly when heated on the water-bath, but remains unchanged when boiled with dilute sodium hydroxide. It shows the same behaviour towards cold and hot glacial acetic acid as the methylamine derivative, but forms the monoacetate melting at 102° when boiled with acetic anhydride.

The *methylaniline* derivative, $NMePh\cdot CH_2\cdot C_6H_2Br(CHO)\cdot OH$, crystallises from benzene, melts at 116—117°, and remains unchanged when boiled with dilute alkali hydroxides. The *pyridine* compound, $OH\cdot C_6H_3(CHO)\cdot CH_2\cdot C_5NH_5Br$ $[OH : CHO : CH_2 = 6 : 1 : 3]$, is obtained as a white powder and melts at 188—190°.

3-*Bromo*-5-*nitro*-4-*hydroxybenzyl bromide*, $OH\cdot C_6H_2Br(NO_2)\cdot CH_2Br$, formed by bromination of Stoermer and Behn's *m*-nitro-*p*-hydroxybenzyl alcohol (Abstr., 1901, i, 726) in hot glacial acetic acid solution, crystallises from petroleum in sheaves of long, slender, yellow needles, melts at 89—90°, is soluble in cold benzene, chloroform, or acetone, and loses hydrogen bromide when treated with alcohol or aqueous acetone. The *monoacetate*, $OH{\cdot}C_6H_2Br(NO_2){\cdot}CH_2{\cdot}OAc$, formed by boiling the benzyl bromide with sodium acetate in glacial acetic acid solution, crystallises in small, glistening, yellow prisms and plates, melts at 112—113°, and is converted by boiling acetic anhydride into the *diacetate*, $OAc{\cdot}C_6H_2Br(NO_2){\cdot}CH_2{\cdot}OAc$, which forms colourless, glistening needles and melts at 58—59°. The *methylamine* derivative, $NMe[CH_2{\cdot}C_6H_2Br(NO_2){\cdot}OH]_2$, is orange-red, melts at 184—185°, and remains unchanged when heated on the water-bath, boiled with aqueous sodium hydroxide, or treated with cold glacial acetic acid. It is only slightly decomposed, yielding traces of methylamine when boiled with glacial acetic acid, and when heated with acetic anhydride forms an *acetyl* derivative which melts at 156° and on hydrolysis yields the methylamine derivative.

The *diethylamine* derivative, $NEt_2{\cdot}CH_2{\cdot}C_6H_2Br(NO_2){\cdot}OH$, crystallises in orange-yellow prisms or long, thin leaflets, melts at 164—165°, is readily soluble in acetone, but more sparingly so in benzene or methyl or ethyl alcohol, and remains unchanged when heated on the water-bath or treated with glacial acetic acid, but is partially resinified when boiled with aqueous alkali hydroxides. It forms the monoacetate melting at 112—113° when boiled with glacial acetic acid, and yields diethylamine when heated with acetic anhydride.

The *diamylamine* derivative, $N(C_5H_{11})_2{\cdot}CH_2{\cdot}C_6H_2Br(NO_2){\cdot}OH$, crystallises in glistening, orange-yellow leaflets, melts at 129—129·5°, and remains unchanged when heated on the water-bath, boiled with alcoholic-aqueous sodium hydroxide, or treated with cold glacial acetic acid. It yields the monoacetate melting at 112—113°, and the diacetate melting at 58—59°, when boiled with glacial acetic acid and acetic anhydride respectively. G. Y.

Certain Derivatives of Phenylglycine-*o*-sulphonic Acid. HAMILTON BRADSHAW (*Amer. Chem. J.*, 1906, **35**, 340—346).—*Phenylglycine-o-sulphonic acid*, $SO_3H{\cdot}C_6H_4{\cdot}NH{\cdot}CH_2{\cdot}CO_2H$, obtained by the action of formaldehyde and hydrogen cyanide on aniline-*o*-sulphonic acid, is a crystalline substance; its *potassium hydrogen* salt is sparingly soluble in cold water. p-*Bromophenylglycine*-o-*sulphonic acid*, obtained in a similar manner, forms flaky crystals, is very soluble in water, and yields a methyl ester; its *potassium hydrogen* salt crystallises in needles.

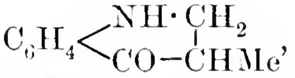
Attempts were made to effect condensations of *p*-bromophenylglycine-*o*-sulphonic acid with production of substances analogous to indigo, but without success. When potassium *p*-bromophenylglycine-*o*-sulphonate was treated with fuming sulphuric acid, it was decomposed with formation of *p*-bromoaniline-*o*-sulphonic acid. By the action of acetic anhydride on the potassium salt, a soluble product was obtained which was probably a sulphonic acid in which acetylation had taken place in the imino-group. Attempts to prepare a normal ester of *p*-bromophenylglycine-*o*-sulphonic acid by the action of methyl iodide were unsuccessful. When potassium hydrogen *p*-bromophenylglycine-*o*-sulphonate was heated with sodamide, no condensation product could be obtained. E. G.

Nitriles of Arylglycines. HANS BUCHERER and ANDRÉ GROLÉE (*Ber.*, 1906, **39**, 986—1013. Compare Abstr., 1902, i, 533).—A number of nitriles of arylglycines have been prepared by (1) the condensation of aromatic amine hydrochlorides with aldehydes or ketones or their derivatives and solid potassium cyanide, suspended in benzene, ether, or light petroleum and (2) the condensation of ketonecyanohydrins with amines in the same solvents. A table is given showing the substances used and the percentage yields of the products obtained.

The condensation products of aniline hydrochloride with ethyl acetoacetate and potassium cyanide and of *m*-xylidine hydrochloride with acetone and potassium cyanide are extremely unstable.

When fused with sodium ethoxide and potassium hydroxide at 270°, anilino*iso*butyric acid, obtained by hydrolysis of the nitrile, prepared by the condensation of aniline with acetonecyanohydrin (Tiemann and Friedländer, Abstr., 1882, 56), yields a *substance*, $C_{10}H_{11}ON$, which crystallises in small, white prisms, sublimes at 110° in glistening prisms, melts at 150—151°, and forms a dye when coupled with *p*-nitrophenyldiazonium chloride. If the acid is an *α*-anilino-compound, the product of fusion must be 2 : 2-dimethylindoxyl,

$$C_6H_4{<}{\substack{NH\\CO}}{>}CMe_2,$$

but 3-methyldihydro-4-carbostyril,  $C_6H_4{<}{\substack{NH\cdot CH_2\\ CO-CHMe}}$, if derived from *β*-anilino*iso*butyric acid (Bischoff and Mintz, Abstr., 1892, 1338).

α-Anilino-*α*-phenylpropionitrile melts at 155—156° (m. p. 152°, Jacoby, Abstr., 1886, 800).

α-o-*Toluidino*iso*butyronitrile*, $C_{11}H_{14}N_2$, crystallises in very pale violet needles, melts at 78—79°, and decomposes readily. The *amide*, $C_{11}H_{16}ON_2$, melts at 131—132°.

α-*o*-Toluidinophenylacetonitrile crystallises in rose-coloured leaflets and melts at 72—73° (m. p. 71°, Sachs, Abstr., 1901, i, 272). The *amide*, $C_{15}H_{16}ON_2$, crystallises in small, white needles, melts at 125—126°, and on hydrolysis with concentrated hydrochloric acid yields the acid melting at 142—143°.

α-p-*Toluidino*iso*butyronitrile*, $C_{11}H_{14}N_2$, crystallises in slender, glistening needles and melts at 73—74°. The *amide* crystallises in slender, white needles and melts at 141—143°.

α-p-*Toluidinophenylacetamide*, $C_{15}H_{16}ON_2$, crystallises in glistening leaflets and melts at 113—114°.

The condensation of *p*-toluidine hydrochloride and *p*-nitrobenzaldehyde in presence of potassium cyanide leads to the formation of *p*-nitrobenzylidene-*p*-toluidine, melting at 124—125°.

p-Aminophenol condenses with acetone and potassium cyanide, or with acetonecyanohydrin, to form a *product*, $C_{10}H_{12}ON_2$, which crystallises in small, glistening, almost white leaflets, melts at 137°, is soluble in aqueous sodium hydroxide, and decomposes quickly on exposure to the air.

α-*p*-Hydroxyanilinophenylacetonitrile (Sachs and Goldmann, Abstr., 1902, i, 780) crystallises in slender, light yellow needles and melts at 113—114°. The *amide*, $OH\cdot C_6H_4\cdot NH\cdot CHPh\cdot CO\cdot NH_2$, crystallises in small needles and melts at 142°.

The *nitrile*, $C_{11}H_{14}ON_2$, prepared from *p*-anisidine and acetonecyanohydrin, melts at 47—48° and is very unstable.

α-*p*-Anisidinophenylacetonitrile melts at 73—74° (m. p. 85°, von Miller, Plöchl, and Scheitz, Abstr., 1899, i, 128).

The *nitrile*, prepared by the condensation of *p*-phenylenediamine hydrochloride, acetone, and potassium cyanide, crystallises in small needles, melts at 157—158°, and decomposes when dried in a desiccator.

The condensation of *p*-phenylenediamine hydrochloride, benzaldehyde, and potassium cyanide leads to the formation of *p*-phenylenediaminodiphenylacetonitrile, melting at 163° (Sachs and Goldmann, *loc. cit.*).

m-*Tolylenediaminodiïsobutyronitrile*, $C_6H_3Me(NH\cdot CMe_2\cdot CN)_2$, crystallises in small, glistening needles, melts at 85—86°, and when coupled with *p*-nitrophenyldiazonium chloride forms a yellow dye. The *amide* crystallises in small, white, nodular aggregates and melts at 200°.

Amino-m-*tolylamino*iso*butyronitrile*, $NH_2\cdot C_6H_3Me\cdot NH\cdot CMe_2\cdot CN$, crystallises in white, unstable needles, melts at 90—91°, and becomes brown on exposure to air. The *amide* melts at 169°. When coupled with *p*-nitrophenyldiazonium chloride, the nitrile forms a reddish-yellow *dye*, $C_{17}H_{18}O_2N_6$, having a characteristic grey lustre, and when heated with concentrated sulphuric acid yielding a dark brown *substance*,

$$\begin{array}{l} C(NH_2){:}CH\cdot C{:}N\cdot CH\cdot CHMe\cdot CO_2H \\ \quad | \qquad\qquad\quad | \qquad\quad | \\ CMe{=\!=}CH\cdot C{:}N\cdot N\cdot C_6H_4\cdot NO_2 \end{array}$$

Benzidinodiïsobutyronitrile, $C_{20}H_{22}N_4$, crystallises from a mixture of alcohol and ether. The *amide* forms small, glistening leaflets and melts above 255°.

The product of the condensation of phenylhydrazine with acetonecyanohydrin is α-phenylhydrazino*iso*butyronitrile, as it does not condense with carbon disulphide or with a second mol. of acetonecyanohydrin (compare Reissert, Abstr., 1884, 1152; Eckstein, Abstr., 1893, i, 85).

The condensation of phenylhydrazine with ethyl acetoacetatecyanohydrin leads to the formation of 1-phenyl-3-methylpyrazolone, melting at 127°.

The *nitrile*, $C_{14}H_{14}N_2$, prepared from α-naphthylamine hydrochloride and acetonecyanohydrin, crystallises in colourless needles, which become bluish-violet on exposure to air, melts at 63—64°, and is readily decomposed by water or dilute hydrochloric acid. The *amide*, $C_{14}H_{16}ON_2$, crystallises in small, white needles and melts at 129—130°.

β-*Naphthylamino*iso*butyronitrile*, $C_{14}H_{14}N_2$, is obtained as a crystalline powder, melts at 106—107°, is more stable than the α-compound, and on hydrolysis yields Bischoff and Mintz's β-naphthylamino*iso*butyric acid, melting at 187—188° (*loc. cit.*). The *amide* crystallises in small, glistening, white leaflets, becomes brown on exposure to air, melts at 168—169°, and dissolves in alcohol to form a fluorescent solution.

β-*Naphthylaminophenylacetamide*, $C_{18}H_{16}ON_2$, forms a white, crystalline powder and melts at 158—159°. The *acid*, $C_{18}H_{15}O_2N$, melts at 175—176°.

The condensation of phenol with benzaldehyde and potassium cyanide in benzene solution leads to the formation of *phenoxyphenylacetamide*, OPh·CHPh·CO·NH$_2$, which melts at 139—140°, and when treated with concentrated sulphuric acid undergoes isomeric change, forming *hydroxydiphenylacetamide*, OH·C$_6$H$_4$·CHPh·CO·NH$_2$, melting above 255°.

Resorcinol condenses with benzaldehyde and potassium cyanide, yielding a yellowish-brown, amorphous *product*, which contains carbon, hydrogen, and oxygen and melts above 255° or when heated with water. G. Y.

New Oxidation Products of Unsymmetrical Disubstituted Aromatic Thiocarbamides. K. DOST (*Ber.*, 1906, **39**, 1014—1016. Compare Hofmann and Gabriel, Abstr., 1892, 1109). —The action of sulphur chloride on *as*-phenylmethylthiocarbamide in chloroform solution leads to the formation of a *hydrochloride*, $C_{16}H_{16}N_4S_2,2HCl$, which crystallises in slender, white needles and melts above 275°. The *base*, which may have the constitution

$$\begin{array}{l} N{:}C(NPhMe)\cdot S \\ | \qquad\qquad\qquad\quad | \\ N{:}C(NPhMe)\cdot S \end{array}$$

or NPhMe·CS·N:N·CS·NPhMe, crystallises in large, white needles and melts at 128°. The *picrate*, $C_{16}H_{16}N_4S_2,2C_6H_3O_7N_3$, crystallises in flocculent aggregates of needles and melts at 230°; the *nitrite*, $C_{16}H_{16}N_4S_2,2HNO_2$, crystallises in matted, orange needles, commences to become red at 120°, and detonates at 153°.

The *base*, $C_{18}H_{20}N_4S_2$, obtained in the same manner from *as*-phenylethylthiocarbamide, crystallises in glassy, nodular aggregates and melts at 86°. The *hydrochloride*, melts at 253°; the *nitrite* forms red, hair-like needles and melts at 152°.

The *product*, $C_{26}H_{20}N_4S_2$, obtained from *as*-diphenylthiocarbimide, crystallises in shining, transparent prisms, melts at 150—210°, and does not form salts. G. Y.

Molecular Rearrangement of Unsymmetrical Diacyl-ψ-thiocarbamides to Isomeric Symmetrical Derivatives. TREAT B. JOHNSON and GEORGE S. JAMIESON (*Amer. Chem. J.*, 1906, **35**, 297—309).—as-*Dibenzoyl-ψ-methylthiocarbamide*, NBz$_2$·C(SMe):NH, obtained by adding benzoyl chloride to a solution of ψ-methylthiocarbamide in presence of potassium hydroxide, crystallises in needles, melts at 130—135° and evolves a small quantity of methyl mercaptan, then solidifies, and, on further heating, partially melts at 145—146° and decomposes at 175—185°. The compound is decomposed by sodium hydroxide solution into benzoic acid and benzoyl-ψ-methylthiocarbamide; it is also decomposed by boiling hydrochloric acid with formation of benzoic acid and an oily product containing sulphur. When this unsymmetrical ψ-thiocarbamide is heated for twenty minutes at 150°, it is converted into s-*dibenzoyl-ψ-methylthiocarbamide*,

$NHBz \cdot C(SMe) \colon NBz$, which crystallises in long, slender needles and melts at 147—148°; the same rearrangement takes place when an alcoholic solution of the unsymmetrical compound is submitted to prolonged boiling. When the symmetrical derivative is boiled with hydrochloric acid, it is converted into methyl mercaptan and *s*-dibenzoylcarbamide.

as-*Dibenzoyl-ψ-ethylthiocarbamide*, $NBz_2 \cdot C(SEt) \colon NH$, melts partially at 104—105°, then solidifies completely, and afterwards melts at 110°. It is decomposed by sodium hydroxide or hydrochloric acid into benzoic acid and benzoyl-ψ-ethylthiocarbamide. When heated at its melting point, the compound undergoes rearrangement into *s-dibenzoyl-ψ-methylthiocarbamide*, $NHBz \cdot C(SEt) \colon NBz$, which crystallises in needles and melts at 110—111°. The symmetrical derivative is soluble in sodium hydroxide solution and is reprecipitated on neutralising with hydrochloric acid; it is decomposed by boiling hydrochloric acid into ethyl mercaptan and *s*-dibenzoylcarbamide.

By the action of *p*-bromobenzoyl chloride on ψ-methylthiocarbamide, s-*di*-p-*bromobenzoyl-ψ-methylthiocarbamide*,

$$C_6H_4Br \cdot CO \cdot NH \cdot C(SMe) \colon N \cdot CO \cdot C_6H_4Br,$$

is obtained, which crystallises in needles and melts at 178°; probably a small quantity of the unsymmetrical compound is also produced. When the symmetrical derivative is heated at its melting point, a small quantity of mercaptan is evolved, but otherwise the compound remains unaltered. It is decomposed by sodium hydroxide with formation of *p*-bromobenzoic acid; it is very stable towards hydrochloric acid, but when boiled with hydrobromic acid is converted into methyl mercaptan and *s*-di-*p*-bromobenzoylcarbamide, which melts and decomposes at 228—233°.

p-*Bromobenzoylcarbamide*, $C_6H_4Br \cdot CO \cdot NH \cdot CO \cdot NH_2$, obtained by the action of *p*-bromobenzoyl chloride on carbamide, forms microscopic crystals, melts and decomposes at 236—237°, and is slightly soluble in alcohol or water.

p-*Methoxybenzoyl-ψ-methylthiocarbamide*,

$$OMe \cdot C_6H_4 \cdot CO \cdot NH \cdot C(SMe) \colon NH,$$

prepared by the action of anisyl chloride on ψ-methylthiocarbamide, crystallises in colourless, slender prisms, melts at 103—105°, and is very soluble in alcohol.

When ψ-methylthiocarbamide is treated with anisyl chloride (2 mols.), a product is obtained which is probably a mixture of as- and s-*di*-p-*methoxybenzoyl-ψ-methylthiocarbamides*. The symmetrical compound, $OMe \cdot C_6H_4 \cdot CO \cdot NH \cdot C(SMe) \colon N \cdot CO \cdot C_6H_4 \cdot OMe$, crystallises in needles, melts at 159—160°, and by the action of boiling hydrochloric acid is converted into methyl mercaptan and dianisylcarbamide, melting at 205—207°.

E. G.

Quinonoid *aci*-Nitrophenol Esters. ARTHUR HANTZSCH and H. GORKE (*Ber.*, 1906, 39, 1073—1084).—From the products of the reaction between anhydrous alkyl haloids and the carefully dried silver salts of nitrophenols below 18°, the authors have isolated, in addition to the ordinary ethers, which in the pure state are quite colourless, intensely-coloured *aci*-nitrophenol esters to the extent of

1—1·5 per cent., to which the structure $O:C_6H_4:NO\cdot OR$ is ascribed. The isomerides are separated by rapidly evaporating the solution in anhydrous ether in a vacuum over sulphuric acid; the indistinctly crystalline, red deposit on the sides of the vessel is separated from the less-intensely coloured well-defined crystals on the bottom of the beaker, dissolved in chloroform, and light petroleum is added drop by drop, causing a precipitation of the true ether. The ester, which remains in solution, has not been obtained pure, and still contains about 10 per cent. of nitrophenol ether.

Ethyl aci-*trinitrophenol ester*, $O:C_6H_2(NO_2)_2:NO\cdot OEt$, containing about 10 per cent. of the isomeric ether, is obtained from silver picrate and ethyl bromide. It forms an indistinctly crystalline red mass, melts at 50—52°, is unimolecular, dissolves readily in ether, alcohol, benzene, or chloroform, and is sparingly soluble in light petroleum. The dry solid changes within two months into the isomeric ether; the same change takes place more rapidly in anhydrous non-hydrolysing solvents, and almost instantaneously when hydrogen chloride, ammonia, or zinc dust is added to such solutions. Water and other hydrolysing solvents instantly destroy the red colour of the ester, this being due partly to the transformation into the ether, partly to hydrolysis and formation of picric acid.

Methyl aci-*trinitrophenol ester*, $O:C_6H_2(NO_2)_2:NO\cdot OMe$, melts between 40° and 42°.

Methyl aci-o-*nitrophenol ester*, $O:C_6H_4:NO\cdot OMe$, is a dark red liquid at the ordinary temperature, solidifying at $-5°$. It is decidedly more stable than the *aci*-trinitrophenol ester, can be preserved for a long time without loss of colour, and is comparatively slowly hydrolysed by water.

Ethyl aci-2 : 4-*dinitrophenol ester*, $O:C_6H_3(NO_2):NO\cdot OEt$, is a very unstable red solid.

Similar compounds obtained from *p*-nitrophenol, 3 : 4-dinitronaphthol, and possibly *m*-nitrophenol were detected by colour reactions but were not isolated and analysed. C. S.

Constitution and Colour of Nitrophenols. ARTHUR HANTZSCH (*Ber.*, 1906, **39**, 1084—1105).—Mainly a discussion of the results mentioned in the previous abstract.

Nitrobenzene, obtained by nitrating pure benzene from benzoic acid, is rendered quite colourless by repeated fractionation, but becomes yellow again when kept. The three dinitrobenzenes, 1 : 2 : 4- and 1 : 3 : 5-trinitrobenzene, trinitrotoluene, trinitroxylene, and trinitrocumene are obtained colourless by repeated crystallisation; β-nitronaphthalene separates from dilute alcoholic solution, after the use of animal charcoal, in colourless plates.

The author claims that all nitrophenol ethers, which are incapable of exhibiting tautomerism, are colourless, and, in accordance with this view, has prepared colourless specimens of trinitroanisole and trinitrophenetole by repeatedly shaking the dry ethereal solution of these ethers with sodium hydrogen carbonate until the colour has disappeared, rapidly evaporating the ether in a current of dry air, and allowing the residue to remain over phosphoric oxide; the colourless crystals, which have the same melting point as the yellow form, are shown to be "optically" colourless in Koenig's spectrophotometer.

The ethereal solution of trinitrophenol acetate, obtained by the action of dry silver picrate on acetyl chloride dissolved in anhydrous ether, is "optically" colourless, and by evaporation over phosphoric oxide deposits colourless crystals, melting at 76° (compare Tommasi and David, this Journal, 1873, 1238) and rapidly turning yellow in the presence of water-vapour.

o-Nitroanisole, obtained from freshly-prepared, dried, and air-free materials, is rendered "optically" colourless by repeated distillation in a high vacuum; the melting point is 9·4°, 0·3° higher than that of the ordinary yellow ether. The corresponding acetate is also easily obtained in a colourless condition from absolute ethereal solution.

Nitrophenol derivatives, which are structurally incapable of exhibiting tautomerism, not only do not exercise selective absorption, but also remain "optically" colourless at varying temperatures and in different solvents, whereas the free nitrophenols under the same conditions exhibit a distinct change of colour. *p*-Nitrophenols and *a*-nitronaphthol show very little tendency to pass into the coloured *aci*-form; on the contrary, this tendency is so great with *o*-nitrophenols that they have not yet been obtained colourless.

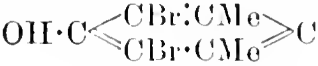
m-Nitrophenol, 2 : 4-dinitrophenol, and picric acid have been obtained free from colour. Marckwald's "colourless" picric acid (Abstr., 1900, i, 391), when examined spectrophotometrically, is found to absorb violet rays; hence under all conditions picric acid contains the *aci*-form.

By a somewhat crude method, the amount of coloured *aci*-form existing in solid solution in the colourless nitrophenols is estimated at not more than about 1 per cent. even in the case of the intensely-coloured *o*-nitrophenol. An exact method of estimation is due to H. Gorke (*Diss.*, Leipzig, 1905).

Assuming that in alkaline solution the nitrophenols are completely in the *aci*-form, the author shows that with increasing dilution the percentage of coloured ions in an aqueous solution of a nitrophenol, colorimetrically determined, increases *pari passu* with the degree of electrolytic dissociation. The more the coloured, dissociated *aci*-nitrophenols change into the undissociated molecules, so much the more real colourless nitrophenol is produced. C. S.

New Brominated ψ-Phenols. KARL AUWERS [and, in part, F. JESCHECK, OTTO SCHRÖTER, TH. MARKOVITS, and C. ROEVER] (*Annalen*, 1906, **344**, 271—280).—3 : 5-*Dibromo*-4-*hydroxy*-2 : 6-*dimethylbenzyl bromide* (s-*dibromo*-p-*hydroxyhemellithyl bromide*),

$$\mathrm{OH{\cdot}C}\begin{array}{l}\diagup\mathrm{CBr{:}CMe}\diagdown\\ \diagdown\mathrm{CBr{\cdot}CMe}\diagup\end{array}\mathrm{C{\cdot}CH_2Br},$$

is prepared by the action of bromine on the corresponding phenolic alcohol in chloroform solution cooled by ice; it crystallises from glacial acetic acid in glistening leaflets, from benzene in slender needles, melts at 140—142°, and is readily soluble in most solvents with the exception of petroleum. As a ψ-phenol, it is insoluble in aqueous alkali hydroxides, and shows the typical reactivity of the α-bromine atom. When reduced with zinc and much concentrated hydrochloric acid, it yields a small amount of impure *dibromohemellithenol*,  $OH\cdot C{<}\genfrac{}{}{0pt}{}{CBr{:}CMe}{CBr\cdot CMe}{>}CMe$, which melts at 172°. The *acetate*,

$$OAc\cdot C_6Me_2Br_2\cdot CH_2Br,$$

formed from the ψ-phenol, crystallises from alcohol or glacial acetic acid in glistening leaflets, melts at 151—158°, and when boiled with aniline in benzene solution yields the *aniline* derivative,

$$OAc\cdot C{<}\genfrac{}{}{0pt}{}{CBr{:}CMe}{CBr\cdot CMe}{>}C\cdot CH_2\cdot NHPh\,;$$

this crystallises in stout, glistening prisms, melts at 145—146°, is insoluble in aqueous alkali hydroxides, and is hydrolysed by digestion with an alcoholic alkali hydroxide, forming *dibromo*-p-*hydroxyhemellithylaniline*, $OH\cdot C_6Me_2Br_2\cdot CH_2\cdot NHPh$, which is formed also by the action of aniline on the ψ-phenol in benzene solution. It crystallises from dilute alcohol or light petroleum in slender, glistening needles and melts at 146·5°.

Dibromo-p-*hydroxyhemellithyl acetate*, $OH\cdot C_6Me_2Br_2\cdot CH_2\cdot OAc$, formed by boiling the bromide with sodium acetate and glacial acetic acid, crystallises in short prisms, melts at 122—123°, is readily soluble in benzene, alcohol, or glacial acetic acid, and when boiled with methyl alcohol for one hour, or digested with methyl alcohol at the ordinary temperature for twenty-four hours, yields the *methyl ether*,

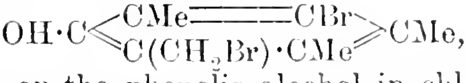
$$OH\cdot C_6Me_2Br_2\cdot CH_2\cdot OMe,$$

which crystallises in long, slender needles and melts at 103°. The action of aqueous acetone on the acetate leads to the formation of the *alcohol*, $OH\cdot C_6Me_2Br_2\cdot CH_2\cdot OH$, which crystallises in matted long, slender needles, melts at 179°, and is readily soluble in alcohol, acetone, ethyl acetate, or glacial acetic acid. The *diacetate*, $C_{13}H_{14}O_4Br_2$, crystallises in stellate aggregates of needles and melts at 122—124·5°.

Dibromo-o-*hydroxymesityl bromide*,  $CBr{<}\genfrac{}{}{0pt}{}{CMe{=\!=}CBr}{CMe{:}C(OH)}{>}C\cdot CH_2Br$, is obtained in a yield of 80—90 per cent. of the theoretical when *o*-hydroxymesityl alcohol cooled by ice, is treated with an excess of bromine; it crystallises in colourless needles, melts at 149—150°, and is insoluble in aqueous alkali hydroxides. The *monoacetate*,

$$OH\cdot C_6Me_2Br_2\cdot CH_2\cdot OAc,$$

separates from dilute methyl alcohol as a colourless powder, melts at 96—97°, and when finely divided is readily soluble in very dilute sodium hydroxide, but if treated with only moderately dilute sodium hydroxide is converted into the amorphous ψ-phenol, which is insoluble in aqueous alkali hydroxides. The *diacetyl* derivative, $C_{13}H_{14}O_4Br_2$, crystallises from light petroleum in long, slender needles or stout prisms and melts at 98—99°.

o-*Hydroxy*iso*duryl bromide*,  $OH\cdot C{<}\genfrac{}{}{0pt}{}{CMe{=\!=\!=}CBr}{C(CH_2Br)\cdot CMe}{>}CMe$, is prepared by the action of bromine on the phenolic alcohol in chloroform solution; it crystallises from a mixture of benzene and petroleum in stout, glistening prisms, is readily soluble in ether, chloroform, or glacial acetic acid, and is insoluble in aqueous alkali hydroxide, but on treatment with alcohol is converted into the phenol, which is soluble in alkali hydroxides. G. Y.

Dinaphthylene Dioxide. Archibald A. Neil (*Ber.*, 1906, **39**, 1059—1060).—*Dinaphthylene dioxide*, $C_{20}H_{12}O_2$, obtained as a by-product in the preparation of 2 : 3-dihydroxynaphthalene, crystallises from toluene in large, pearly leaflets and sublimes in colourless plates. Its solution in toluene has a slight violet fluorescence. The *compound*, $C_{20}H_{11}O_3$, also obtained as a by-product in the same preparation, forms colourless needles, dissolves in sodium hydroxide, and melts at 209—212° (compare Ullmann and Stein, this vol., i, 258).

A. McK.

Onocerin (Onocol). Franz von Hemmelmayr (*Monatsh.*, 1906, **27**, 181—198. Compare Thoms, Abstr., 1897, i, 201, 361).—When oxidised with chromic acid in glacial acetic acid solution at the ordinary temperature, onocol yields onoketone and *onoceric acid*, $C_{20}H_{30}O_4$. This melts to a resinous mass under boiling water; when dry, some preparations melted at 70—80°, others at 100—120°; it is readily soluble in alcohol, ether, benzene, or glacial acetic acid, becomes strongly electrified when rubbed, and is probably dibasic. The *silver* salt, $C_{20}H_{29}O_4Ag$, was analysed; the *barium* salt decomposes when washed with water. If the oxidation takes place in hot glacial acetic acid solution, *ψ-onoceric acid*, which contains a greater percentage of carbon than is required by the formula $C_{20}H_{30}O_4$, is formed; it resembles onoceric acid, and melts slowly after becoming soft at 80°. A diminution of the percentage of carbon in the acid product is observed if an excess of chromic acid is used either in cold or hot solution. The author could not obtain Thoms' acid, $C_{20}H_{40}O_2$ (*loc. cit.*).

When oxidised with nitric acid, onocol yields traces of acetic and butyric acids together with amorphous nitro-acids; if cold fuming nitric acid is used, the chief product is *dinitro-onoceric acid*, $C_{20}H_{28}O_4(NO_2)_2$, which is obtained as a yellow powder and melts and decomposes at about 180°. With hot concentrated nitric acid, yellow, amorphous *trinitro-onoceric acid*, $C_{20}H_{27}O_4(NO_2)_3$, melting and decomposing at 210—220°, is obtained.

Small amounts of acetic and butyric acids are formed also by the oxidation of onocol with chromic acid in concentrated sulphuric acid solution. Potassium permanganate has little action on onocol in neutral or alkaline solution, but in presence of an acid oxidises it completely to carbon dioxide and water. G. Y.

Hydrogenation of Cholesterol. Carl Neuberg (*Ber.*, 1906, **39**, 1155—1158. Compare Diels and Abderhalden, this vol., i, 272).—On reducing cholesterol with sodium in boiling amyl alcohol, a *dihydrocholesterol*, $C_{27}H_{46}O$, is obtained with a yield of 30—50 per cent.; it separates from alcohol in small, white, prismatic crystals, and after drying in a vacuum over phosphoric oxide melts at a temperature between 119° and 124°, depending on the rate of heating. It does not respond to the Salkowski or Obermüller tests, and differs from the parent cholesterol in being dextrorotatory, having $[\alpha]_D$ +18·35° in

10 per cent. ethereal solution. Whether it is identical with natural coprosterol remains to be investigated. W. A. D.

Reduction of *a-iso*Dypnopinacolin. F. V. Daels (*Bull. Acad. roy. Belg.*, 1905, 585—601).—When *a-iso*dypnopinacolin (Abstr., 1900, i, 603, 604) is reduced with sodium amalgam in alcohol, it furnishes, in addition to unidentified products, benzaldehyde, triphenylbenzene, and an *alcohol*, $C_{32}H_{28}O$, melting at 184°. When the reduction is effected by means of zinc dust and acetic acid, a better yield of the same alcohol is obtained, and it is accompanied by an *isomeride* which melts at 178°.

The alcohol, $C_{32}H_{28}O$, crystallises from alcohol or acetic acid in colourless needles, is not esterified by acetyl or benzoyl chloride, does not react with hydroxylamine or phenylhydrazine, and is not dehydrated when boiled for several days with acetic acid. A mixture of hydrochloric and acetic acids converts it into a *hydrocarbon*, $C_{32}H_{26}$, which crystallises in short, slender needles, melts at 180°, is not reduced by sodium amalgam in alcohol, and sublimes when heated under reduced pressure, for the most part unchanged. When distilled under reduced pressure, the alcohol is partially decomposed, yielding (1) a volatile liquid, probably identical with that produced by the distillation of dypnone (Abstr., 1900, i, 35), (2) a yellow resin having a strong odour of benzaldehyde, and (3) a semi-liquid brown resin containing some triphenylbenzene. When warmed with a dilute alcoholic solution of potassium hydroxide, it is converted into a third *isomeric alcohol*, which crystallises from acetic acid, benzene, or alcohol in colourless needles, melts at 162°, is without action on phenylhydrazine or hydroxylamine, and when heated with a mixture of hydrochloric and acetic acids, or with acetyl chloride, is dehydrated, yielding the hydrocarbon $C_{32}H_{26}$ already noted. When distilled under reduced pressure, the same products are obtained as from the first isomeride.

The second alcohol, melting at 178°, obtained in the initial reaction, crystallises in lamellæ, is soluble in boiling acetic acid, and less so in boiling alcohol. When distilled under reduced pressure, it furnishes the same products as the two isomerides already described.

T. A. H.

Hofmann's Reaction. III. Ernst Mohr (*J. pr. Chem.*, 1906, [ii], **73**, 228—238. Compare Abstr., 1905, i, 890; this vol., i, 252).—When prepared by Graebe and Rostovzeff's method (Abstr., 1902, i, 633), benzoylchloroamide is obtained as a sandy powder, which, after purification by solution in aqueous potassium hydroxide and precipitation with acetic acid, melts at 113—115°. It interacts with 1 mol. of potassium hydroxide according to the equation: $NHCl\cdot COPh + KOH = NPh{:}CO + KCl + H_2O$, or with 2 mols. according to the equation: $NHCl\cdot COPh + 2KOH = NHPh\cdot CO_2K + KCl + H_2O$. If in the usual scheme representing the course of Hofmann's reaction: $NH_2\cdot COPh \longrightarrow NHCl\cdot COPh \longrightarrow NCl{:}CPh\cdot OK \longrightarrow NPh{:}CCl\cdot OK (IV) \longrightarrow$

$$NPh{:}C(OH)\cdot OK (V) \longrightarrow NHPh\cdot CO_2K (VI) \longrightarrow NH_2Ph,$$

substances V and VI are the tautomeric forms of the phenylcarbamate, substance IV is now the only hypothetical intermediate product.

G. Y.

Formation of Amides and Hydrolysis of Esters by Amides. Hans Meyer (*Monatsh.*, 1906, **27**, 31—48).—The action of aqueous ammonia on an ester leads to the formation of the amide or to hydrolysis of the ester and formation of the ammonium salt; this, which is formed more often than is usually supposed (Hofmann, Abstr., 1882, 950; Einhorn and Konek, Abstr., 1893, i, 445), is the product of the interaction of ammonium hydroxide and the ester. The action of anhydrous gaseous or liquid ammonia on esters leads to the formation of a mixture of products (Tingle, Abstr., 1900, i, 641; 1901, i, 200). The action of alcoholic ammonia on esters is reversible, and with an excess of alcohol the formation of the ester may be the chief reaction even at temperatures below 100° (Kirpal, Abstr., 1901, i, 227). Digestion with concentrated aqueous ammonia in a closed vessel at the laboratory temperature or at 100° remains the best method of converting esters into amides.

When heated with saturated alcoholic ammonia at 125° for three hours, ethyl benzoate yields 16·8 per cent. (Fischer and Dilthey, Abstr., 1902, i, 269), but on digestion with aqueous ammonia of sp. gr. 0·910 at the laboratory temperature for forty-eight hours, 60·8 per cent. of the theoretical amount of benzamide. Under the same conditions, 75 and 82 per cent., respectively, of the theoretical yield of phenylacetamide are obtained from ethyl phenylacetate.

The action of ammonia on an ester leads to the formation, in the first instance, of an additive compound, $R\cdot C(OH)(OEt)\cdot NH_2$, and the reaction must take place therefore the more readily the stronger the acid, that is, the more negative the group R. Thus ethyl trichloroacetate interacts readily with ammonia to form the amide, whereas trimethylacetamide is not obtained from the ester. The formation of the amide may be hindered also by the presence of other substituting groups.

3-*Methylcinchonyl chloride*, formed by boiling 3-methylcinchonic acid with thionyl chloride, crystallises in nodular aggregates of almost colourless needles and melts at 175°. *Methyl 3-methylcinchonate*,

$$C_9NH_5Me\cdot CO_2Me,$$

formed by the action of methyl alcohol on the acid chloride, or of diazomethane on the acid, crystallises in colourless needles, melts at 77°, remains unchanged when digested with alcoholic ammonia at the laboratory temperature, and is hydrolysed completely by aqueous ammonia at 130°.

3-*Methylcinchonamide*, $C_9NH_5Me\cdot CO\cdot NH_2$, is formed from the acid chloride; it separates from alcohol in dull, colourless crystals, melts at 229—230°, is hydrolysed only slowly by boiling 10 per cent. aqueous potassium hydroxide, and remains unchanged when heated with aqueous ammonia at 130° for three hours.

Ethyl 2-hydroxy-1-naphthoate remains unchanged when digested with aqueous ammonia at the laboratory temperature for some weeks, but is decomposed when heated at 100° for some hours, forming chiefly β-naphthol and ammonium carbamate. The amide, formed by the thionyl chloride method (Abstr., 1902, i, 31), remains unchanged when heated with aqueous ammonia at 100°. The methyl esters of the fatty acids interact with ammonia to form the corresponding amides, more easily than do the ethyl esters (compare Hofmann, *loc. cit.*; van Linge Abstr., 1897, i, 618).

The corresponding amides were obtained from the following methyl esters, in yields of the percentages of the theoretical given: methyl *n*-butyrate, 84 per cent.; methyl *iso*butyrate, 91 per cent.; methyl valerate, 78 per cent.; methyl hexoate, 45 per cent.; methyl arachate, about 15 per cent. Under the same conditions, hexoamide was obtained from the ethyl ester in a yield of only 3 per cent. of the theoretical.

Methylmalonamide is obtained in a yield of 93 per cent., dimethylmalonamide in a yield of 81 per cent., when the corresponding dimethyl esters are digested with aqueous ammonia at the laboratory temperature for twelve and twenty-four hours respectively. Dimethyl diethylmalonate remains unchanged when digested with aqueous ammonia (compare this vol., i, 137). G. Y.

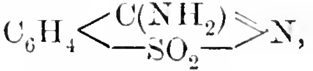
Linking of Amino-acids. Ernst Mohr and Friedrich Köhler (*Ber.*, 1906, **39**, 1057—1058).—*o*-Aminobenzoylanthranilic acid, $NH_2·C_6H_4·CO·NH·C_6H_4·CO_2H$, prepared from its sodium salt, obtained by the interaction of phthalimide, sodium hydroxide, and sodium hypochlorite in aqueous solution, crystallises in needles and melts at 202—203°. Its acetyl derivative melts at 223—224° (compare Anschütz, Schmidt, and Greiffenberg, Abstr., 1903, i, 57).

A. McK.

***o*-Sulphaminebenzoic Acid and Related Compounds.** Hamilton Bradshaw (*Amer. Chem. J.*, 1906, **35**, 335—340).—Wilson (Abstr., 1904, i, 51) has found that *o*-sulphaminebenzoic acid crystallises either in plates or needles. A study has been made of the conditions under which each of these forms is produced.

The compound, melting at 263°, which was obtained by Wilson (*loc. cit.*) by the action of ammonium thiocyanate on *o*-sulphaminebenzoic acid is not the diamide, but is ammonium *o*-carbaminebenzenesulphonate.

By the action of phosphorus oxychloride on potassium *o*-carbaminebenzenesulphonate, Wilson (*loc. cit.*) obtained a compound which he regarded as *o*-carbaminebenzenesulphonic chloride. By treating the same potassium salt with phosphorus pentachloride, Sohon (Abstr., 1898, i, 429) obtained *o*-cyanobenzenesulphonic chloride, a compound which was also obtained by Jesurun (Abstr., 1893, i, 715) by heating benzoic sulphinide with phosphorus pentachloride. It has now been found that the same chloride, melting at 69—70°, is obtained by each of the three methods. Jesurun's results on the action of ammonia on *o*-cyanobenzenesulphonic chloride (*loc. cit.*) have been confirmed except with regard to the melting points. "ψ-Saccharinamide,"



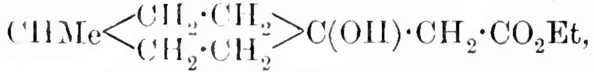
$$C_6H_4<\begin{matrix}C(NH_2)\\ SO_2\end{matrix}>N,$$

melts at 297° (uncorr.). *o*-Cyanobenzenesulphonamide melts at 160° (uncorr.) and is simultaneously converted into "ψ-saccharinamide."

When *o*-cyanobenzenesulphonamide is heated with dilute sodium hydroxide, it is converted into benzoicsulphinide.

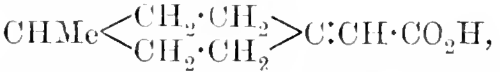
By the action of sodium hypobromite on potassium *o*-carbaminebenzenesulphonate, aniline-*o*-sulphonic acid is produced. E. G.

Optically-active Substances which do not contain an Asymmetric Atom. Willy Marckwald and Richard Meth (*Ber.*, 1906, 39, 1171—1177. Compare Perkin and Pope, *Proc.*, 1906, 22, 107).—1-Methyl*cyclo*hexane-4-one combines with ethyl iodoacetate or ethyl bromoacetate in presence of magnesium, giving *ethyl* 1-*methyl*cyclo*hexane-4-ol-4-acetate*,



$$\mathrm{CHMe}<\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{C(OH)\cdot CH_2\cdot CO_2Et},$$

which on hydrolysis gives rise to two *acids*, which are probably *cis* and *trans* isomerides; *a*-1-*methyl*cyclo*hexane*-4-*ol*-4-*acetic acid* is sparingly soluble in water and melts at 140—141°, the isomeric *β-acid* being much more soluble in water and melting at 78—81°. Both acids when heated with 30 per cent. sulphuric acid give rise to the same 1-*methyl*cyclo*hexylidene*-4-*acetic acid*,



$$\mathrm{CHMe}<\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{C{:}CH\cdot CO_2H},$$

which, when purified by means of the *barium* salt, melts at 40·5—41°; this acid is sparingly soluble in water, reduces potassium permanganate, when heated with aqueous potassium hydroxide gives 4-methylhexanone, and with cinchonine yields a *salt*, $C_{19}H_{21}ON_2,2C_9H_{14}O_2$, which is sparingly soluble in light petroleum and melts at 56—63°. This salt on being decomposed with dilute sulphuric acid gives d-1-*methyl*cyclo*hexylidene*-4-*acetic acid*, which has $[\alpha]_D$ + 9·3°. The light petroleum mother liquors of the cinchonine salt give the l-1-*methyl*cyclo*hexylidene*-4-*acetic acid* with $[\alpha]_D$ − 10·4°.

The authors have repeated the work of Erlenmeyer, jun. (Abstr., 1905, i, 892; this vol., i, 21, 176) with cinnamic acid and have failed to confirm his results; on preparing in alcoholic solution the brucine salt of cinnamic acid from storax, the salt melting at 107—113° could alone be obtained, with a specific rotatory power $[\alpha]_D$ − 16·5° to − 19·5°. The same salt was obtained from synthetical cinnamic acid. W. A. D.

Note.—Perkin and Pope (*loc. cit.*) have prepared 1-methyl*cyclo*hexylidene-4-acetic acid by another method; their product is not identical with the acid described above. W. A. D.

Relative Rates of Oxidation of ortho-, meta-, and para-Compounds. Hamilton Bradshaw (*Amer. Chem. J.*, 1906, 35, 326—335).—Determinations have been made of the relative rates of oxidation of the following substances by potassium permanganate at the ordinary temperature: *o*-, *m*-, and *p*-hydroxybenzoic acids; *o*-, *m*-, and *p*-aminobenzoic acids; *o*-, *m*-, and *p*-nitrophenols; *o*-, *m*-, and *p*-nitroanilines, and *o*-, *m*-, and *p*-toluidines. The results are tabulated.

When the hydroxybenzoic acids are treated with a neutral solution of potassium permanganate, the ortho-compound is the most readily oxidised and the para-compound the least. The influence of alkali hydroxide and of sulphuric acid on the rate of oxidation of these acids was studied, and it was found that the effect of the alkali hydroxide depends only on its concentration and not on the actual quantity present. Since, during the oxidation of organic substances, potassium hydroxide is formed by the reduction of the permanganate, and becomes neutralised to a greater or less extent by the acid products of the oxidation, it was considered more satisfactory to use solutions containing a considerable amount of potassium hydroxide. Under these conditions, the order of the velocity of oxidation was, in all cases, meta, ortho, para, the meta-compounds being oxidised the most rapidly and the para-compounds the least. E. G.

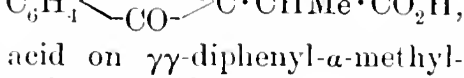
Preparation of Salicylic Acid from *o*-Cresol, and a New Method of preparing Aurin. CHRISTIAN RUDOLPH (*Zeit. angew. Chem.*, 1906, **19**, 384—385).—When a solution of *o*-cresol in concentrated sodium hydroxide is heated under pressure at 170—190° in the presence of sodium chromate, a deep red solution is obtained resembling an alkaline solution of rosolic acid; the reaction is probably due to the oxidation of some of the *o*-cresol to salicylic aldehyde, which then condenses with two more mols. of *o*-cresol to form a trihydroxytriphenylmethane. Aurin was prepared by heating a solution of 108 grams of *p*-cresol and 188 grams of phenol in 400 grams of 32 per cent. sodium hydroxide with a solution of 300 grams of sodium dichromate in 250 grams of 32 per cent. sodium hydroxide for some hours under pressure at 180°. The aurin was extracted from the mixture by means of sodium hydrogen sulphite.

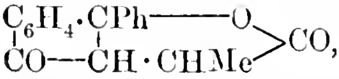
P. H.

Indoneacetic Acids. III. "Indonisation" and "Anhydrisation." HANS STOBBE and FERDINAND GOLLÜCKE (*Ber.*, 1906, **39**, 1066—1069. Compare Abstr., 1902, i, 542; 1904, i, 503).—The action of acetyl chloride on γγ-diphenyl-α-methylitaconic acid,

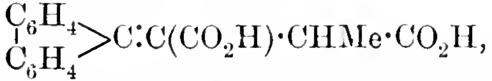
$$CPh_2{:}C(CO_2H){\cdot}CHMe{\cdot}CO_2H,$$

is analogous with that on diphenylitaconic acid itself, *γγ-diphenyl-α-methylitaconic anhydride*, $C_{18}H_{14}O_3$, being formed; it separates from carbon disulphide in prisms and melts at 146°.

γ-Phenyl-α-indonepropionic acid,  $C_6H_4{<}\begin{matrix}CPh\\CO\end{matrix}{>}C{\cdot}CHMe{\cdot}CO_2H$, prepared by the action of sulphuric acid on γγ-diphenyl-α-methylitaconic acid, has an orange colour and melts at 168°. Its solution in concentrated sulphuric acid is dark green.

The *lactone* of *3-hydroxy-3-phenyl-1-hydrindone-2-propionic acid*,  $\begin{matrix}C_6H_4{\cdot}CPh\text{——}O\\CO\text{—}CH{\cdot}CHMe\end{matrix}{>}CO$, obtained as a by-product of the action of sulphuric acid on γγ-diphenyl-α-methylitaconic acid, separates from ether in colourless plates and from chloroform in prisms; it melts at 94°. Its solution in sodium hydroxide is first yellow and then becomes orange.

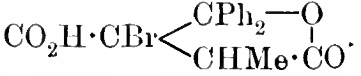
γγ-Diphenylene-α-methylitaconic acid,



$$\begin{matrix}C_6H_4\\C_6H_4\end{matrix}{>}C{:}C(CO_2H){\cdot}CHMe{\cdot}CO_2H,$$

prepared by the condensation of fluorenone with ethyl pyrotartrate in the presence of sodium ethoxide, separates from chloroform in yellow crystals and melts and decomposes at 158°. The *anhydride*, prepared from it by the action of acetyl chloride, is yellow and melts at 147—148°. It does not form an indone compound when treated with sulphuric acid. A. McK.

$\gamma\gamma$-Diphenyl-α-methylitaconic Acid. HANS STOBBE and MAX NOETZEL (*Ber.*, 1906, **39**, 1070—1072. Compare preceding abstract). —$\gamma\gamma$-Diphenyl-α-methylitaconic acid (Abstr., 1896, i, 234) in chloroform solution does not react with bromine in diffused daylight; the addition takes place readily when cold water is added, a dibromide being produced which loses hydrogen bromide spontaneously to form *β-bromo-$\gamma\gamma$-diphenyl-α-methylparaconic acid*,



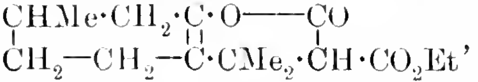
$CO_2H\cdot CBr<\begin{matrix}CPh_2—O\\ |\\ CHMe\cdot CO\end{matrix}$.

The latter melts and decomposes at 174·5° and, when heated or boiled with water, loses hydrogen bromide to form the stable *$\gamma\gamma$-diphenyl-α-methylaconic acid*,

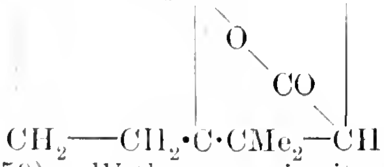
$CO_2H\cdot C<\begin{matrix}CPh_2\cdot O\\ |\\ CMe-CO\end{matrix}$, which separates from water in prisms and melts at 180—181°. The *calcium* and *silver* salts are described. A. McK.

Additive Processes. DANIEL VÖRLANDER (*Annalen*, 1906, **345**, 155—250. Compare Abstr., 1903, i, 495, 632; 1904, i, 65; 1905, i, 792).—Recent observations by various investigators, which throw light on the existence of two types of compounds, the unstable A type and the relatively more stable B type (*loc. cit.*), are discussed. The two series of salts of trialkyltrimethylenetriamine (Einhorn and Prettner, Abstr., 1904, i, 978) appear to illustrate this phenomenon remarkably clearly. The linking of carbon with carbon belongs in general to the B type, but Gomberg's triphenylmethyl appears to yield a hexaphenylethane of the A type.

[With FRANZ KÖTHNER.]—*Pulegone and Alkyl Sodiomalonates.*— Pulegone and ethyl sodiomalonate react in benzene solution, yielding the *anhydride* of the *monoethyl* ester of *pulegonemalonic acid*,



$\begin{matrix}CHMe\cdot CH_2\cdot C\cdot O——CO\\ |\qquad\qquad\ \ ||\qquad\qquad |\\ CH_2—CH_2—C\cdot CMe_2\cdot CH\cdot CO_2Et\end{matrix}$, which can be isolated by a careful series of fractional distillations as an oil boiling at 193—195° under 20 mm. and at 201—205° under 24 mm. pressure; it decolorises bromine slowly, hydrogen bromide being evolved and a brown, unstable oil produced. When hydrolysed, it yields the ketodilactone (pulegonemalonicdilactone),



$\begin{matrix}CHMe\cdot CH_2\cdot C—O——CO\\ |\qquad\quad O\qquad |\\ |\qquad\quad CO\qquad |\\ CH_2——CH_2\cdot C\cdot CMe_2—CH\end{matrix}$, melting at 104° (Abstr., 1899, i, 259). With ammonia it yields the anhydride of pulegoneacetamide (m. p. 141—143°). Methyl sodiomalonate yields the corresponding *methyl* ester of the anhydride of pulegonemalonic acid, $C_{14}H_{20}O_4$; it is isolated by fractional distillation under reduced pressure and crystallises from petroleum in needles melting at 75—76°, and has $[\alpha]_D$ in methyl-alcoholic solution = $+26\cdot0—26\cdot6°$ at 20°.

Hydrolysis of either of the esters of the anhydride affords a very good method of preparing the ketodilactone, details of which are given; this substance has $[\alpha]_D$ $+13\cdot0°$ at 33° in alcoholic solution, and 13·73° at 20° in chloroform solution. Menthone, $C_{10}H_{18}O$, boiling at 98—99° under 19 mm. pressure, is also a by-product of the reaction.

Ethyl pulegonemalonate,

$$CHMe{<}{\substack{CH_2—CO\\CH_2\cdot CH_2}}{>}CH\cdot CMe_2\cdot CH(CO_2Et)_2,$$

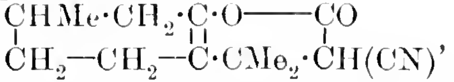
prepared by heating an alcoholic solution of the pulegonemalonicdilactone with sulphuric acid, is purified by careful fractionation of the crude product, and is an oil boiling at 209—210° under 25 mm. pressure, and has $[\alpha]_D$ $-3\cdot27°$ at 20° in alcoholic solution. In the reaction, pulegone and ethyl malonate are formed; ethyl pulegoneacetate is also produced, carbon dioxide being at the same time evolved. *Methyl pulegonemalonate* is obtained in a similar manner, and forms crystals melting at 51° and boiling at 187—188° under 15 mm. pressure, and has $[\alpha]_D$ $-8\cdot74—8\cdot79°$ at 20° in methyl-alcoholic solution.

Both esters are partially decomposed by sodium methoxide or ethoxide respectively into pulegone and the alkyl malonate, an equilibrium: pulegone + alkyl sodiomalonate + alcohol $\rightleftarrows$ alkyl pulegonemalonate + sodium ethoxide, being established. The medium greatly affects the point of equilibrium, in benzene the additive product being mainly formed, in alcohol pulegone and malonic ester. Very little addition takes place at a higher temperature.

With ammonia, the esters give a mixture of the anhydride of pulegoneacetamide and the monoamide of pulegonemalonic acid. The latter melts at 125°, at the same time losing water and carbon dioxide, becoming converted into the amide-anhydride.

On distilling the barium salt of pulegonemalonic acid, prepared from the ketodilactone and barium hydroxide, pulegone is alone formed.

The *anhydride* of *pulegonecyanoacetic acid*,

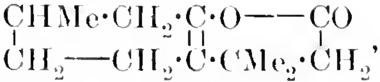


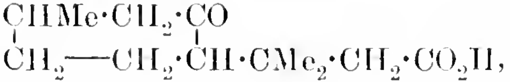
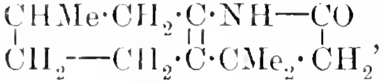
$$\begin{array}{l}CHMe\cdot CH_2\cdot C\cdot O——CO\\ \;|\qquad\qquad\quad\;\; ||\qquad\quad\;\; |\\ CH_2—CH_2—C\cdot CMe_2\cdot CH(CN)'\end{array}$$

prepared from pulegone, ethyl cyanoacetate, and sodium in the presence of benzene, and then hydrolysing the product with potassium hydroxide, is purified by fractional distillation under reduced pressure, and crystallises in prisms melting at 75—76°; it reduces permanganate and decolorises bromine immediately. It is converted by alcoholic ammonia into the *amideanhydride* of pulegonecyanoacetic acid, which forms rhombic crystals, subliming without melting above 300°, a sublimate of prismatic needles being formed. If the product of the interaction of pulegone and ethyl cyanoacetate is heated with alkali hydroxide and then acidified, pulegonemalonicdilactone is formed.

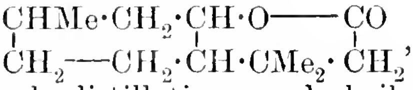
When pulegone is boiled with an alcoholic solution of sodium ethoxide, a substance, $C_{20}H_{30}O$ (?), is formed, which can be isolated by fractional distillation under reduced pressure; it is a pale yellow oil with a green fluorescence, boiling at 200—204° under 20 mm. pressure and having $[\alpha]_D$ $+30\cdot23—30\cdot92°$ at 20° in alcoholic solution. It is probably a condensation product.

[With ALFRED MAY and WILHELM KÖNIG.]—*Pulegoneacetic Acid.*—

The *anhydride* of pulegoneacetic acid,  $\begin{array}{l}\mathrm{CHMe{\cdot}CH_2{\cdot}C{\cdot}O{-}{-}CO}\\ \mathrm{CH_2{-}{-}CH_2{\cdot}C{\cdot}CMe_2{\cdot}CH_2}\end{array}$, is prepared from pulegonemalonicdilactone, which is heated until the evolution of carbon dioxide ceases, and then distilled under reduced pressure, when it boils at 178° under 30 mm. pressure; it crystallises in prismatic needles melting at 44°, has $[\alpha]_D$ +71·13—71·61° at 20° in alcoholic solution, and decolorises bromine and permanganate immediately, in the latter case hydrobromic acid being evolved.

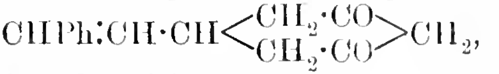
Pulegoneacetic acid,  $\begin{array}{l}\mathrm{CHMe{\cdot}CH_2{\cdot}CO}\\ \mathrm{CH_2{-}{-}CH_2{\cdot}CH{\cdot}CMe_2{\cdot}CH_2{\cdot}CO_2H}\end{array}$, is prepared by treating the anhydride with alcoholic potassium hydroxide and subsequently liberating the acid from the potassium salt; it forms colourless crystals melting at 67—68° and has $[\alpha]_D$ −2·6—3·2° at 20° in alcoholic solution. When heated at 130°, the anhydride is formed, the same reaction being brought about more easily in the presence of acetic anhydride. The *anhydride* of pulegoneacetamide,  $\begin{array}{l}\mathrm{CHMe{\cdot}CH_2{\cdot}C{\cdot}NH{-}{-}CO}\\ \mathrm{CH_2{-}{-}CH_2{\cdot}C{\cdot}CMe_2{\cdot}CH_2}\end{array}$, is formed when the anhydride of pulegoneacetic acid is treated with ammonia, or when the pulegonemalonicdilactone is heated with alcoholic ammonia under pressure; it crystallises in needles melting at 140—141° and has $[\alpha]_D$ +65·88—65·99° at 20° in alcoholic solution. The anhydride yields crystalline derivatives with ethylamine and phenylhydrazine.

The *semicarbazone* of pulegoneacetic acid, prepared from the acid and semicarbazide, forms white crystals melting and decomposing at 186—188°. *Methyl pulegoneacetate*, prepared from the anhydride and methyl alcohol in the presence of sulphuric acid, is an oil boiling at 155—157° under 24 mm. pressure and having $[\alpha]_D$ −6·58—6·88° at 20° in methyl-alcoholic solution. The *ethyl* ester boils at 166·5—169° under 25 mm. pressure and has $[\alpha]_D$ −0·8—1·13° at 20° in alcoholic solution. Both esters are converted into the anhydride of pulegoneacetamide by treatment with ammonia.

When pulegonemalonicdilactone is reduced with sodium and alcohol, an *anhydride* of *pulegolacetic acid*,  $\begin{array}{l}\mathrm{CHMe{\cdot}CH_2{\cdot}CH{\cdot}O{-}{-}CO}\\ \mathrm{CH_2{-}{-}CH_2{\cdot}CH{\cdot}CMe_2{\cdot}CH_2}\end{array}$, is formed; it is purified by fractional distillation, and boils at 175—180° under 16 mm. pressure; at low temperatures, it solidifies in crystals which melt at 33° and has $[\alpha]_D$ +18·21° at 20° in alcoholic solution. With barium hydroxide, the anhydride is converted into *barium pulegolacetate*, $(C_{12}H_{21}O_3)_2Ba$.

On reducing the anhydride of pulegoneacetic acid with sodium and alcohol, a second *anhydride* of pulegolacetic acid, stereoisomeric with that just described, is formed; it forms colourless crystals melting at 54°, and boils at 167° under 22 mm. pressure, and has $[\alpha]_D$ + 21·65° at 20° in alcoholic solution; at the same time, menthone is formed, which distils over in the first fraction. Further, in the residue left after the distillation of the anhydride, a substance is contained which distils at 168—170° under 22 mm. pressure and has $[\alpha]_D$ +16·5° at 20° in alcoholic solution.

Pulegonemalonicdilactone and pulegone- and pulegol-acetic anhydrides yield with excess of alkali hydroxides the corresponding salts of the acetates; solutions of these salts are slowly converted into the anhydrides and alkali hydroxide.

[With Paul Groebel.]—*Addition of Malonic Ester to Cinnamylideneacetone and Ethyl Cinnamenylacrylate.*—Cinnamylideneacetone and ethyl sodiomalonate combine to form hydroresorcinol derivatives, the constitutions of which depend on whether the ethyl malonate becomes attached to the $\alpha\beta$-, the $\alpha\delta$-, or the $\gamma\delta$-positions in the group $C:C\cdot C:C\cdot C:O$; the constitution can be determined by oxidising these derivatives first with bleaching powder and then oxidising the unsaturated dicarboxylic acid with permanganate, when certain acids will be produced which will determine the constitution of the original material. Since tricarballylic and benzoic acids are produced, it follows that the original additive product was a cinnamenyldihydroresorcin,  $CHPh:CH\cdot CH<\begin{matrix}CH_2\cdot CO\\ CH_2\cdot CO\end{matrix}>CH_2$, the addition having taken place in the $\alpha\beta$-position.

A similar addition takes place in the case of ethyl cinnamenylacrylate.

Cinnamenyldihydroresorcin was prepared by reducing cinnamylideneacetone with ethyl malonate in absolute alcoholic solution in the presence of sodium ethoxide; the sodium salt of ethyl cinnamenyldihydroresorcylate, which is first formed, is hydrolysed with sodium carbonate and the free acid obtained on acidifying boiled until the evolution of carbon dioxide ceases; the compound crystallises in colourless needles melting at 186°. *Cinnamenylglutaric acid*,

$$CHPh:CH\cdot CH(CH_2\cdot CO_2H)_2,$$

is obtained by oxidising an alkaline solution of the compound just mentioned with bleaching powder; it crystallises in lustrous leaflets melting at 134—135°. The *dimethyl* ester prepared from the acid and methyl alcohol in the presence of sulphuric acid crystallises in slender needles melting at 69—70°. *Cinnamenylglutaric anhydride*, prepared by heating the acid for several hours with acetic anhydride, which is subsequently distilled, crystallises in needles sintering at 135° and melting at 138°. If the anhydride is treated with aniline in a benzene solution, the *anilido-acid*, $CHPh:CH\cdot CH(CH_2\cdot CO\cdot NHPh)\cdot CH_2\cdot CO_2H$, is obtained as needles sintering at 139° and melting at 142°.

The cinnamenylglutaric acid was oxidised by alkaline permanganate solution, which was immediately decolorised, the odour of benzaldehyde becoming apparent. The excess of permanganate is removed by hydrogen peroxide, the liquid neutralised by acetic acid, and lead acetate added to precipitate the lead tricarballylate; benzoic acid is obtained from the mother liquor. The tricarballylic acid was completely identified by conversion into the anhydro-acid and into the anilido-acid, which it forms with *o*-toluidine.

Ethyl cinnamenylacrylate reacts with ethyl malonate in the presence of sodium ethoxide in alcoholic solution, giving a compound which, heated at 160°, yields β-cinnamenylglutaric acid (m. p. 134°). Methyl cinnamenylacrylate, prepared from the acid and methyl alcohol in the presence of acetic acid, crystallises in leaflets melting at 71°.

[With Hermann Staudinger.]—*Cinnamylideneacetophenone and*

Ethyl Sodiomalonate.—Cinnamylideneacetophenone readily reacts with ethyl sodiomalonate in ethereal solution, forming *ethyl cinnamylideneacetophenonemalonate*, $CHPh{:}CH{\cdot}CH(CH_2{\cdot}COPh){\cdot}CH(CO_2Et)_2$, which crystallises in needles melting at 92—93°. The corresponding *acid* is readily obtained from the ester by hydrolysis, and crystallises in needles melting at 163°, carbon dioxide being at the same time evolved. *Cinnamylideneacetophenoneacetic acid*,

$$CHPh{:}CH{\cdot}CH(CH_2{\cdot}COPh){\cdot}CH_2{\cdot}CO_2H,$$

prepared by heating the corresponding acid at 165—170°, crystallises in needles melting at 125°. The *ethyl* ester crystallises in needles melting at 75—76°. When oxidised by an alkaline solution of permanganate, the acid last mentioned yields a mixture of benzoic and phenacylsuccinic acids.

Cinnamylideneacetophenone and ethyl acetoacetate condense in ethereal solution, forming the *compound* $C_{23}H_{22}O_3$, which crystallises in needles melting and decomposing at 142—143°. When the ester is hydrolysed, a *compound* $C_{20}H_{18}O$, which is also produced in the original condensation, is obtained; it crystallises in needles melting at 106°.

[With Paul Weissheimer and Fritz Sponnagel.]—*Ethyl Sorbate and Ethyl Sodiomalonate.*—In the formation of the condensation-product of ethyl sorbate and ethyl sodiomalonate, the addition takes place at the $\alpha\delta$-position, the additive product having probably the constitution $CO_2Et{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CHMe{\cdot}CH(CO_2Et)_2$; the condensation is brought about in benzene solution in the presence of sodium hydroxide, but on attempting to isolate the acid formed by hydrolysis of the primary product, carbon dioxide is evolved and *methylheptenedicarboxylic acid* formed. The latter could not be purified, but was converted into the *ethyl* ester, $CO_2Et{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CHMe{\cdot}CH_2{\cdot}CO_2Et$, which boils at 158—160° under 26 mm. pressure; it decolorises a bromine solution and reduces permanganate. When the crude methylheptenedicarboxylic acid was oxidised with permanganate, pyruvic and oxalic acids were alone obtained, although both tricarballylic acid and β-methylglutaric acid were sought for.

All attempts to reduce the dicarboxylic acid to methylpimelic acid, or to condense the diethyl ester with ethyl sodiomalonate, failed.

[With Ernst Strunck.]—*Action of Alkyl Sodiomalonates on $\beta\gamma$-Unsaturated Alkyl Carboxylates.*—A very large number of $\beta\gamma$- and $\gamma\delta$-unsaturated acids and other unsaturated compounds which do not contain a carbonyl group have been tested with respect to their reactivity with ethyl sodiomalonate. It was found that the $\gamma\delta$-unsaturated compounds did not react, whilst of the $\beta\gamma$-substances investigated only ethyl phenyl*iso*crotonate reacted at all readily.

*Ethyl phenyl*iso*crotonate*, $CHPh{:}CH{\cdot}CH_2{\cdot}CO_2Et$, can be prepared from the acid and purified by fractionation; it is an oil boiling at 183° under 30 mm. pressure; it changes on keeping, and gives gradually a coloration with ferric chloride. The ester prepared from the silver salt, on the other hand, can be kept unchanged and gives no coloration with ferric chloride. The *methyl phenyl*iso*crotonate* boils at 180·5° under 20 mm. pressure.

The ester was condensed with ethyl sodiomalonate in benzene solution and the product hydrolysed with potassium hydroxide, a *tricarboxylic acid*, $C_{13}H_{11}O_6$, being formed; it is difficult to obtain in a pure state, and melts with evolution of carbon dioxide at 146°.

β-Benzylglutaric acid, $CH_2Ph\cdot CH(CH_2\cdot CO_2H)_2$, is prepared by heating small quantities of the tricarboxylic acid at 160° and recrystallising the product from water, from which it separates in leaflets melting at 102°. The *diethyl* ester is an oil boiling at 188—189° under 17 mm. pressure; it decolorises permanganate and gives an intense green coloration with ferric chloride, reactions, however, which were traced to a minute trace of impurity present probably in the ethyl phenyl*iso*crotonate. The *anhydride* of *β-benzylglutaric acid* is obtained by heating the acid with acetyl chloride; it melts at 85° and gives no reaction with ferric chloride or permanganate. With α-naphthylamine, it yields an *α-naphthylamido-acid*, which crystallises in needles melting at 154°.

Dilute nitric acid does not attack β-benzylglutaric acid, but the concentrated acid at 60° converts it into a *nitro*-compound, $C_{12}H_{13}O_6N$, which crystallises in needles melting at 163°.

Phenylacetaldehyde condenses with malonic acid in the presence of pyridine, forming a mixture of the *αβ*- and the *βγ*-phenylcrotonic acids. If the condensation is carried out in acetic acid, then the *βγ*-acid is alone formed. Ethyl malonate and phenylacetaldehyde condense in the presence of diethylamine, forming a mixture of substances which, after hydrolysis, lose carbon dioxide and leave a mixture of β-benzylglutaric acid and phenyl-βγ-crotonic acid.

Ethyl βγ-hydropiperate, $C_{14}H_{16}O_4$, prepared from the silver salt, boils at 230° under 45 mm. pressure; it condenses with ethyl sodiomalonate in benzene solution, but only a small quantity of a condensation product could be isolated; it appeared to be identical with the dicarboxylic acid (m. p. 123°) which is formed from ethyl αβ-hydropiperate and ethyl sodiomalonate. *Ethyl αβ-hydropiperate*, prepared from the silver salt, is an oil boiling at 235—240° under 30 mm. pressure; it condenses with ethyl sodiomalonate, yielding a tricarboxylic acid, $C_{15}H_{16}O_8$, which crystallises in needles; at 80° it begins to lose carbon dioxide and is converted into a *dicarboxylic acid*,

$$CH_2{:}O_2{:}C_6H_3\cdot CH_2\cdot CH_2\cdot CH(CH_2\cdot CO_2H)_2,$$

which crystallises in leaflets melting at 125°. K. J. P. O.

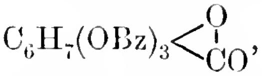
Quinic Acid. P. ECHTERMEIER (*Arch. Pharm.*, 1906, **244**, 37—57). —*Cinchonine, quinidine, cinchonidine, quinine,* and *strychnine quinates* are crystalline and contain each one molecule of the base and one molecule of the acid with 10, 2, 4, 3, and $1H_2O$ respectively; the first four melt, decomposing sometimes as they melt, at 195—196°, 178—179°, 216°, and 187—188° respectively; only the cinchonidine salt crystallises readily.

Methyl quinate, $C_6H_7(OH)_4\cdot CO_2Me$, was prepared by boiling a mixture of methyl iodide and methyl alcohol with silver quinate; it melts at 126° to a milky liquid which clears at 142—143°. An attempt to obtain a phenyl ester by heating a mixture of phenol and the acid with phosphorus oxychloride yielded two products in small quantity, melting at 122° and 151—152° respectively. No definite product was obtained from the methyl ester by the action of ammonia, hydrazine, phenylhydrazine, or aniline.

Tetra-acetylquinic acid (Erwin and Koenigs, Abstr., 1889, 991) forms a crystalline *phenyl* ester, which melts at 167°. No well-defined chloride could be obtained by the action of thionyl chloride on the silver salt.

When quinic acid is heated at 130—140° with three times its weight of benzoyl chloride, *tetrabenzoylquinic acid*,

$$C_6H_7(OBz)_4\cdot CO_2H,2H_2O$$

(only $1H_2O$ is lost at 95°; the *sodium* and *silver* salts contain 2 and $3H_2O$ respectively) is formed, together with a crystalline substance, $C_{28}H_{24}O_9$, melting at 107—108°, which probably is a *tribenzoylquinide* containing $1H_2O$. The *ethyl* ester of tetrabenzoylquinic acid, melting at 134°, was prepared, and also the *chloride* in a crude state as a viscous oil. In pyridine solution, the reaction between benzoyl chloride and quinic acid yields a *tribenzoylquinide*,  $C_6H_7(OBz)_3<\overset{O}{\underset{CO}{|}}$, melting at 148°, as the main product. When quinic acid is boiled with benzoyl chloride and a little zinc chloride, *dibenzoylquinol*, $C_6H_4(OBz)_2$, melting at 199°, is obtained, identical with the product of the benzoylation of quinol by the Schotten-Baumann method; below 135—140°, this product is not formed. Unlike the by-products, it is not soluble in ether; consequently its ready formation from quinic acid probably affords the most convenient means of detecting this acid.

By treating quinic acid with a solution of phosphoric oxide in (cooled) nitric acid of sp. gr. 1·5, a *product* was obtained which melted at 157°, contained nitrogen, and was acid in reaction. C. F. B.

Condensation of Dibenzyl Ketone with *p*-Nitro-, *p*-Hydroxy-, *p*-Chloro-, and *o*-Nitro-benzaldehydes. LEOPOLD SCHIMETSCHEK (*Monatsh.*, 1906, 27, 1—12. Compare Hertzka, Abstr., 1905, i, 291).—*Chloro-*p*-nitrobenzyldibenzyl ketone* (*δ-chloro-αγ-diphenyl-δ-*p*-nitrophenyl-β-butanone*), $CH_2Ph\cdot CO\cdot CHPh\cdot CHCl\cdot C_6H_4\cdot NO_2$, formed by the action of hydrogen chloride on a benzene solution of dibenzyl ketone and *p*-nitrobenzaldehyde, cooled by ice, crystallises in matted, glistening, white needles, melts at 143°, is readily soluble in ether or benzene, but only sparingly so in methyl or ethyl alcohol, and remains unchanged on prolonged boiling or heating in a sealed tube at 100° with alcohol. The *phenylhydrazone*, $C_{28}H_{24}O_2N_3Cl$, crystallises in long, reddish-yellow prisms and melts at 168°. p-*Nitrobenzylidenedibenzyl ketone* [*αγ-diphenyl-δ-*p*-nitrophenyl-Δγ-butylene-β-one*],

$$CH_2Ph\cdot CO\cdot CPh\colon CH\cdot C_6H_4\cdot NO_2,$$

is formed when chloro-*p*-nitrobenzyldibenzyl ketone is heated at 165° under 14 mm. pressure; it crystallises from alcohol in colourless needles and melts at 104°.

*Chloro-*p*-hydroxybenzyldibenzyl ketone* [*δ-chloro-αγ-diphenyl-δ-*p*-hydroxyphenyl-β-butanone*], $CH_2Ph\cdot CO\cdot CHPh\cdot CHCl\cdot C_6H_4\cdot OH$, formed by the action of hydrogen chloride on a mixture of dibenzyl ketone and *p*-hydroxybenzaldehyde dissolved in a small amount of glacial acetic acid, crystallises from ether in white plates, melts, decomposes, and resolidifies at 100°, and melts again at 138°.

p-*Hydroxybenzylidenedibenzyl ketone* [*αγ-diphenyl-δ*-p-*hydroxyphenyl-Δγ-butylene-β-one*], $CH_2Ph\cdot CO\cdot CPh\!:\!CH\cdot C_6H_4\cdot OH$, is formed when chloro-*p*-hydroxybenzyldibenzyl ketone is boiled with methyl or ethyl alcohol or is heated in a vacuum at 145—150°; it crystallises in colourless needles, melts at 139°, and is readily soluble in methyl or ethyl alcohol, but only sparingly so in benzene, toluene, or light petroleum.

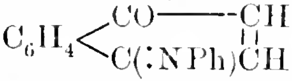
Chloro-p-*chlorobenzyldibenzyl ketone* [*δ-chloro-αγ-diphenyl-δ*-p-*chlorophenyl-β-butanone*], $CH_2Ph\cdot CO\cdot CHPh\cdot CHCl\cdot C_6H_4Cl$, formed from dibenzyl ketone and *p*-chlorobenzaldehyde, crystallises in white plates, melts at 169°, and remains unchanged when boiled with alcohol. When heated at 190° under reduced pressure, it yields hydrogen chloride and p-*chlorobenzylidenedibenzyl ketone* [*αγ-diphenyl-δ*-p-*chlorophenyl-Δγ-butylene-β-one*], $CH_2Ph\cdot CO\cdot CPh\!:\!CH\cdot C_6H_4Cl$, which crystallises in white needles and melts at 128°.

When boiled with phenylhydrazine and acetic acid in alcoholic solution, dichlorobenzyldibenzyl ketone forms 1 : 4-*diphenyl*-5-p-*chlorophenyl*-3-*benzylpyrazoline*,  $NPh<\begin{matrix}N & C\cdot CH_2Ph\\ CH(C_6H_4Cl)\cdot & CHPh\end{matrix}$, which crystallises in long, white prisms, melts at 120—122°, and gives Knorr's pyrazoline reaction.

Chloro-o-*nitrobenzyldibenzyl ketone* [*δ-chloro-αγ-diphenyl-δ*-o-*nitrophenyl-β-butanone*], $CH_2Ph\cdot CO\cdot CHPh\cdot CHCl\cdot C_6H_4\cdot NO_2$, formed from dibenzyl ketone and *o*-nitrobenzaldehyde, crystallises from benzene or alcohol in light yellow needles, melts at 176°, and remains unchanged when boiled with alcohol. The *phenylhydrazone*, $C_{28}H_{24}O_2N_3Cl$, crystallises in dark yellow prisms and decomposes at 142°.

When heated at 200° in a vacuum, chloro-*o*-nitrobenzyldibenzyl ketone yields hydrogen chloride, o-*nitrobenzylidenedibenzyl ketone* [*αγ-diphenyl-δ*-o-*nitrophenyl-Δγ-butylene-β-one*], and traces of phenylacetyl chloride. G. Y.

Formation of Diazoxides and Naphthaquinoneanils from Nitrosobenzene. Hans Euler (*Ber.*, 1906, **39**, 1035—1040).—

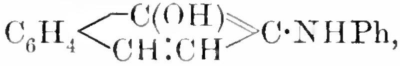
1 : 4-*Naphthaquinoneanil*,  $C_6H_4<\begin{matrix}CO\text{——}CH\\ C(\!:\!NPh)CH\end{matrix}$, is readily formed when an aqueous solution of *α*-naphthol, sodium hydroxide and ammonium chloride is added at 0° to a solution of nitrosobenzene in acetone. A small amount of a *compound*, $C_{22}H_{16}ON_2$, is formed at the same time (see following abstract). The anil crystallises from ether in large, ruby-red prisms and melts at 103°. It dissolves readily in most organic solvents and also in dilute acids, and is readily reduced by zinc and acetic acid to a *leuco*-compound, which is reoxidised when exposed to the air. The *hydrochloride*, $C_{16}H_{12}ONCl$, is insoluble in ether, and when freshly prepared is colourless, but rapidly darkens, and is hydrolysed by water. When boiled with dilute sulphuric acid, the anil is hydrolysed to aniline and 1 : 4-naphthaquinone. The anil is also formed by the action of hydroxylamine on a solution of *α*-naphthol and nitrosobenzene.

1 : 4-*Naphthaquinone*-p-*toluidide*, $C_{17}H_{13}ON$, prepared from nitrosotoluene, *α*-naphthol, and alkali, also crystallises in ruby-red prisms and

melts at 95°. A sparingly soluble compound melting at 176° is formed at the same time.

1 : 2-*Naphthaquinoneanil* is much less stable than the isomeric 1 : 4-compound, and must be immediately removed when once formed, as otherwise it is reduced to a leuco-compound. It crystallises from alcohol in slender, dark green needles, melts at 99—100°, and dissolves readily in most organic solvents. When hydrolysed, it yields aniline and β-naphthaquinone. J. J. S.

Naphthaquinoneanils and their Derivatives. Astrid Euler and Hans Euler (*Ber.*, 1906, **39**, 1041—1045. Compare preceding abstract).—1 : 2-*Naphthaquinolanil* (2-*anilino-α-naphthol*),



$$C_6H_4<\begin{matrix}C(OH)\\CH{:}CH\end{matrix}>C\cdot NHPh,$$

is formed when the clear solution obtained by the action of α-naphthol, sodium hydroxide, and ammonium chloride dissolved in aqueous acetone on an acetone solution of nitrosobenzene is kept for two hours and then poured into water. It crystallises from benzene in colourless scales, melts at 156°, and is readily soluble in most organic solvents. It may also be obtained by reducing 1 : 2-naphthaquinoneanil.

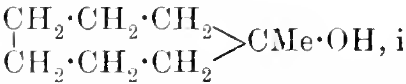
The compound $C_{22}H_{16}ON_2$, obtained as a by-product in the preparation of 1 : 4-naphthaquinoneanil, is shown to be *anilino*-1 : 4-*naphthaquinoneanil*. It melts at 178—179°, is sparingly soluble, and, when hydrolysed with ethyl alcohol and fuming hydrochloric acid at 100°, yields aniline and anilinonaphthaquinone.

When the 1 : 4-naphthaquinoneanil is boiled in aqueous-alcoholic solution with hydroxylamine hydrochloride, it yields a small amount of α-naphthaquinoneoxime melting at 194°, a certain amount of *bis-α-naphthaquinoneoxime*, $OH\cdot N{:}C_{10}H_5O\cdot C_{10}H_5O{:}N\cdot OH$, which forms a red powder, melting above 300° and readily soluble in alkalis, and a considerable amount of *bis*-1 : 4-*naphthaquinoneanil*, $C_{32}H_{20}O_2N_2$, in the form of a purplish-red powder, melting at 233° and readily soluble in benzene.

Nitrosophenol, α-naphthol, and alkali in acetone solution yield a small amount of a *compound*, $C_{16}H_{11}O_3N$, in the form of a minutely crystalline, brown powder, which does not melt below 300°. J. J. S.

Terpenes and Ethereal Oils. LXXVII. New Heptacyclic Compounds. Otto Wallach (*Annalen*, 1906, **345**, 139—154).—By the aid of Grignard's reaction, a number of heptacyclic compounds have been synthesised from suberone.

1-*Methylsuberol*,

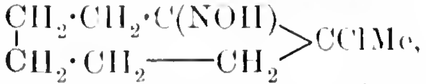


$$\begin{matrix}CH_2\cdot CH_2\cdot CH_2\\|\\CH_2\cdot CH_2\cdot CH_2\end{matrix}>CMe\cdot OH,$$

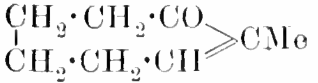
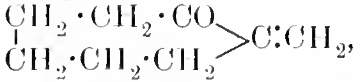
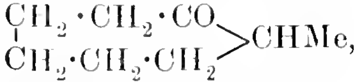
is obtained by the action of magnesium methyl iodide on suberone, and is a thick oil boiling at 183—185°, and having a sp. gr. 0·9285 and n_D 1·4677 at 22°. When heated with potassium hydrogen sulphate in a current of hydrogen, water is eliminated and Δ¹-*methylsuberenone* (1-*methyl*-Δ¹-cyclo-*heptene*),

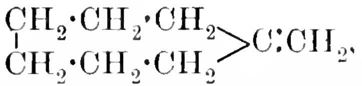
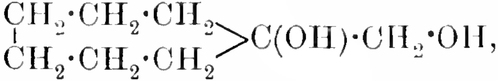
$$\begin{matrix}CH_2\cdot CH_2\cdot CH\\|\\CH_2\cdot CH_2\cdot CH_2\end{matrix}>CMe,$$

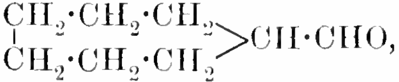
is produced; it boils at 137·5—138·5°, and has a sp. gr. 0·824 and n_D 1·4581 at 19·5°; it is oxidised by dilute potassium permanganate to *ε-acetylhexoic acid*, $CH_2Ac\cdot[CH_2]_4\cdot CO_2H$, which yields a *semicarbazone* melting at 113—114° and is oxidised by sodium hypobromite to pimelic acid. The *nitrosate*, $C_8H_{14}\cdot N_2O_4$, melts and decomposes at 97—98°; the *nitrosochloride*,

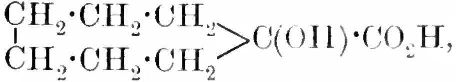


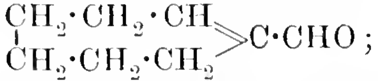
$$\begin{array}{l}CH_2\cdot CH_2\cdot C(NOH)\\ CH_2\cdot CH_2\text{——}CH_2\end{array}\!\!>CClMe,$$

melts at 106°. The nitrosochloride reacts with piperidine, giving the *nitrolamine*, $C_8H_4(NO)\cdot C_5NH_{10}$, melting at 107°. The nitrosate and the nitrosochloride both react with sodium methoxide, the groups NO_3 or Cl being replaced by OMe, *methoxymethylsuberaneoxime* being formed; the latter crystallises in plates melting at 74—75°, and when boiled with acids yields a ketone resembling suberone in odour. *Methylsuberenone*,  $\begin{array}{l}CH_2\cdot CH_2\cdot CO\\ CH_2\cdot CH_2\cdot CH\end{array}\!\!>CMe$ or  $\begin{array}{l}CH_2\cdot CH_2\cdot CO\\ CH_2\cdot CH_2\cdot CH_2\end{array}\!\!>C{:}CH_2$, is prepared from methylsuberene nitrosochloride, from which the hydrochloric acid is eliminated by means of a tertiary base, dimethylaniline; it is purified by conversion into the *semicarbazone*, which melts at 162—163°, boils between 200° and 205°, and has a sp. gr. 0·9695 and n_D 1·4867 at 21°. When reduced with sodium and alcohol, a saturated alcohol is obtained, which is oxidised by chromic acid to *methylsuberone* (1-*methyl*cyclo*heptane-2-one*),  $\begin{array}{l}CH_2\cdot CH_2\cdot CO\\ CH_2\cdot CH_2\cdot CH_2\end{array}\!\!>CHMe$, which was obtained in the form of its *semicarbazone* melting at 129—131°.

Methylenesuberene,  $\begin{array}{l}CH_2\cdot CH_2\cdot CH_2\\ CH_2\cdot CH_2\cdot CH_2\end{array}\!\!>C{:}CH_2$, is obtained from ethyl suberolacetate (Abstr., 1901, i, 156), which is hydrolysed to suberene-acetic acid; on heating, this substance loses carbon dioxide, yielding the methylenesuberene, which resembles very closely the isomeric Δ^1-methylsuberene, above described. Methylenesuberene shows little tendency to absorb oxygen from the air. When oxidised with potassium permanganate, suberone and the *glycol*,  $\begin{array}{l}CH_2\cdot CH_2\cdot CH_2\\ CH_2\cdot CH_2\cdot CH_2\end{array}\!\!>C(OH)\cdot CH_2\cdot OH$, are formed; the latter forms a colourless, crystalline solid which melts at 50—51° and boils at 135—140° under 16 mm. pressure.

When treated with dilute acids, water is immediately eliminated, and a saturated *suberanealdehyde*,  $\begin{array}{l}CH_2\cdot CH_2\cdot CH_2\\ CH_2\cdot CH_2\cdot CH_2\end{array}\!\!>CH\cdot CHO$, produced; it is an oil smelling like benzaldehyde, and forms a *semicarbazone* melting at 153—154° and a solid *oxime* boiling at 110—120° under 11 mm. pressure. The aldehyde is oxidised by silver oxide to heptamethylenecarboxylic acid.

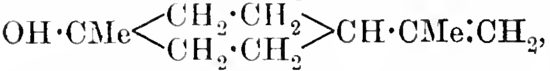
In the oxidation of methylenesuberene by potassium permanganate, *hydroxysuberanecarboxylic acid*,  $\begin{array}{l}CH_2\cdot CH_2\cdot CH_2\\ CH_2\cdot CH_2\cdot CH_2\end{array}\!\!>C(OH)\cdot CO_2H$, is formed together with the glycol; it melts at 78° and is identical with the acid formed from suberonecyanohydrin and from bromo*cyclo*heptanecarboxylic acid; it can be readily purified by means of a well-characterised sodium salt and when warmed with lead peroxide and sulphuric acid is converted into suberone. Methylenesuberene yields a *nitrosochloride* with ethyl nitrite and hydrochloric acid; the compound is not formed so readily as in the case of Δ^1-methylsuberene; it is converted by sodium methoxide into a liquid *oxime*, which is decomposed by sulphuric acid into suberenealdehyde,



$$\begin{matrix}CH_2\cdot CH_2\cdot CH \\ CH_2\cdot CH_2\cdot CH_2\end{matrix}\!>\!C\cdot CHO;$$

its *semicarbazone* crystallises in needles melting at 203—204°. The constitution of the aldehyde was fixed by oxidising it with silver oxide to suberenecarboxylic acid (m. p. 50—51°). K. J. P. O.

Terpenes and Ethereal Oils. LXXVI. New Compounds from β-Terpineol. Otto Wallach [with Ernst Schmitz] (*Annalen*, 1906, **345**, 127—138).—β-Terpineol,

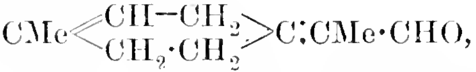


$$OH\cdot CMe\!<\!\begin{matrix}CH_2\cdot CH_2 \\ CH_2\cdot CH_2\end{matrix}\!>\!CH\cdot CMe\!:\!CH_2,$$

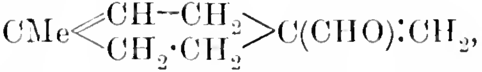
has been shown (Abstr., 1902, i, 803) to combine with nitrosyl chloride, nitrogen peroxide, and nitrogen trioxide. The reactions of these substances have now been studied.

With sodium methoxide, the nitrosochloride yields a *hydroxyoxime*, which could not be obtained in a definite crystalline condition; when boiled with acids, hydroxylamine is eliminated, and a *compound*, $C_{10}H_{14}O$, which is either an aldehyde or ketone according to the origin of the hydroxyoxime, produced.

The *aldehyde*,

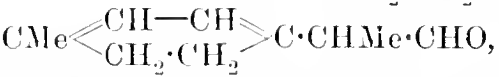


$$CMe\!<\!\begin{matrix}CH-CH_2 \\ CH_2\cdot CH_2\end{matrix}\!>\!C\!:\!CMe\cdot CHO,$$



$$CMe\!<\!\begin{matrix}CH-CH_2 \\ CH_2\cdot CH_2\end{matrix}\!>\!C(CHO)\!:\!CH_2,$$

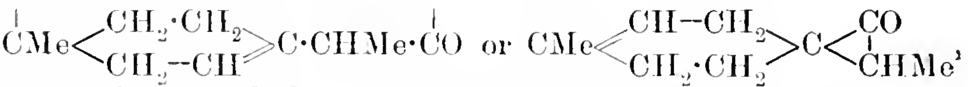
or



$$CMe\!<\!\begin{matrix}CH-CH \\ CH_2\cdot CH_2\end{matrix}\!>\!C\cdot CHMe\cdot CHO,$$

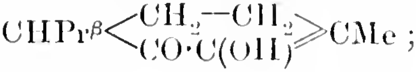
which is the first aldehyde of the terpene series to be synthesised, is prepared by heating the product of the action of sodium methoxide on the nitrosochloride with a saturated solution of oxalic acid; the *semicarbazone* is then prepared and crystallises in leaflets melting at 209°. From the latter, the aldehyde is regenerated by hydrolysis with oxalic acid. It boils at 96° under 11 mm. pressure, and has a sp. gr. 0·97 and n_D 1·4952 at 19°; it reduces silver nitrate, being oxidised to an *acid*, $C_{10}H_{14}O_2$, which crystallises in leaflets melting at 74°. Its *silver* salt, $C_{10}H_{13}O_2Ag$, was analysed.

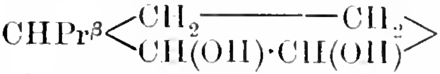
The *ketone*,



$$\overset{|}{C}Me\!<\!\begin{matrix}CH_2\cdot CH_2 \\ CH_2-CH\end{matrix}\!>\!C\cdot CHMe\cdot \overset{|}{C}O \text{ or } CMe\!<\!\begin{matrix}CH-CH_2 \\ CH_2\cdot CH_2\end{matrix}\!>\!C\!<\!\begin{matrix}CO \\ | \\ CHMe\end{matrix},$$

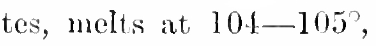
is prepared by hydrolysing the hydroxyoxime with 10 per cent. sulphuric acid instead of oxalic acid, and is purified by conversion into a *semicarbazone* which forms crystals melting at 218°; the latter is converted into the ketone by warming with strong sulphuric acid; it is an oil boiling at 93° under 13 mm. and at 218—220° under the ordinary pressure. It has a sp. gr. 1·001 and n_D 1·4937 at 20°. With hydroxylamine, it yields a solid *oxime* melting at 124—125°. It does not reduce an ammoniacal silver solution, but decolorises bromine and potassium permanganate immediately. K. J. P. O.

Buchu-camphor (Diosphenol), $C_{10}H_{16}O_2$. FRIEDRICH W. SEMMLER and McKENZIE (*Ber.*, 1906, 39, 1158—1170. Compare Shimoyama, Abstr., 1888, 1205; Kondakoff and Bjalobrzeski, Abstr., 1897, i, 227 and 443; Kondakoff and Bachtschéeff, Abstr., 1901, i, 334).—Diosphenol, $C_{10}H_{16}O_2$, obtained from oil of buchu leaves, appears from the following facts to have the structure  $CHPr^{\beta}<\begin{array}{l}CH_2-CH_2\\CO\cdot C(OH)\end{array}>CMe$; it melts when pure at 83—84°, boils at 109—110° under 10 mm. pressure, and is optically inactive.

On reduction with sodium and alcohol, it gives p-*menthane*-2 : 3-*diol*,  $CHPr^{\beta}<\begin{array}{l}CH_2\text{———}CH_2\\CH(OH)\cdot CH(OH)\end{array}>CHMe$, which boils at 135—137° under 10 mm. pressure, has a sp. gr. 0·981 at 20°, and n_D 1·47593; on oxidation with chromic acid, the diol gives a *keto-alcohol*, $C_{10}H_{18}O_2$, which boils at 105—115° under 13 mm. pressure, has a sp. gr. 0·968 at 20°, n_D 1·4616, gives a *semicarbazone* melting at 200°, and when oxidised with potassium permanganate gives α-methyl-δ-*iso*propyladipic acid, melting at 104°. With bromine in glacial acetic acid, diosphenol gives a *dibromo*-derivative, $C_{10}H_{14}Br_2O_2$, and when heated with concentrated hydrochloric acid for two hours at 150—180° it gives thymol nearly quantitatively, a little carvacrol being also formed.

On oxidising diosphenol with ozone in presence of water, γ-acetyl-α-*iso*propyl-*n*-butyric acid, $CH_2Ac\cdot CH_2\cdot CHPr^{\beta}\cdot CO_2H$, is obtained quantitatively, the product being identical with the acid obtained by Semmler (Abstr., 1904, i, 261) and Wallach (Abstr., 1903, i, 566); it melts at 41°, boils at 165° under 14 mm. pressure, has a sp. gr. 1·041 at 20°, n_D 1·45862, and a mol. refraction 45·2 (calc. for a keto-acid, $C_9H_{16}O_3$, 45·6). An alkaline solution of bromine converts γ-acetyl-α-*iso*propyl-*n*-butyric acid into α-*iso*propylglutaric acid, which melts at 94·5° and boils at 202—205°. When diosphenol is oxidised with potassium permanganate in acetone, an *acid*,

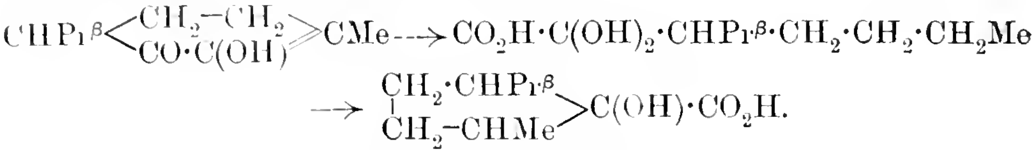
$$CO_2H\cdot CO\cdot CHPr^{\beta}\cdot CH_2\cdot CH_2\cdot COMe,$$

is the first product, but this on distillation in a vacuum loses water and gives an *acid*,  $CO_2H\cdot C<\begin{array}{l}CHPr^{\beta}\cdot CH_2\\CH\text{———}CO\end{array}>CH_2$; the latter crystallises from water in plates, melts at 104—105°, boils at 187—193° under 14 mm. pressure, has a sp. gr. 1·0767 at 20°, n_D 1·47936, and a mol. refraction 47·96 (calc. for the keto-acid, $C_{10}H_{14}O_4$, 47·52). The *oxime*, $C_{10}H_{15}O_3N$, melts at 182°.

The proximity in diosphenol of the hydroxyl group to the carbonyl group modifies the properties of the latter very considerably; diosphenol does not give a semicarbazone nor a phenylhydrazone, although it gives a normal *oxime*, $C_{10}H_{17}O_2N$, melting at 125° (Kondakoff describes the oxime as melting at 156°). Diosphenol behaves, moreover, like an aldehyde with regard to the magenta test and towards Fehling's solution and ammoniacal silver nitrate.

With boiling acetic anhydride containing sodium acetate, diosphenol gives an *acetyl* derivative, $C_{12}H_{18}O_3$, which boils at 138—143° under 13 mm. pressure, has a density 1·034 at 20°, and n_D 1·4848. The *benzoyl* derivative, $C_{17}H_{20}O_3$, boils at 218—219° under 11 mm. pressure, and the *phenylurethane* melts at 41°.

On heating diosphenol with alcoholic potassium hydroxide at 150—160°, the following changes occur:

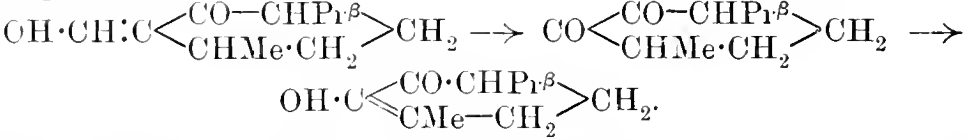


$$CHPr^{\beta}<\begin{matrix}CH_2-CH_2\\ CO\cdot C(OH)\end{matrix}>CMe \longrightarrow CO_2H\cdot C(OH)_2\cdot CHPr^{\beta}\cdot CH_2\cdot CH_2\cdot CH_2Me \longrightarrow \begin{matrix}CH_2\cdot CHPr^{\beta}\\ CH_2-CHMe\end{matrix}>C(OH)\cdot CO_2H.$$

Alcohol-acid, $C_{10}H_{18}O_3$.

The *alcohol-acid*, $C_{10}H_{18}O_3$, crystallises from water in needles, melts at 94°, and boils at 167—168° under 14 mm. pressure; the *methyl* ester, $C_{11}H_{20}O_3$, boils at 104—105° under 13 mm. pressure, has a sp. gr. 1·0008 at 20°, and n_D 1·45512. The *ethyl* ester, $C_{12}H_{22}O_3$, boils at 120° under 12 mm. pressure, has a sp. gr. 0·984 at 20°, and n_D 1·45162. The *acetyl* derivative, $C_{14}H_{24}O_4$, of the ethyl ester boils at 125—130° under 9 mm. pressure, has a sp. gr. 1·01 at 20°, and n_D 1·45112. On oxidising the alcohol-acid, $C_{10}H_{18}O_3$, with lead peroxide in presence of acid, the ketone, $\begin{matrix}CH_2\cdot CHPr^{\beta}\\ CH_2-CHMe\end{matrix}>CO$ (Semmler's *dihydrocamphorphorone*, Wallach's *dihydropulegenone*), is obtained; it boils at 64—65° under 12 mm. pressure, has a sp. gr. 0·893 at 20°, n_D 1·4446, and gives a *semicarbazone*, $C_{10}H_{19}ON_3$, melting at 195°. When the acid, $C_{10}H_{18}O_3$ is heated with hydrochloric acid at 150—160°, it gives rise to a *compound*, $C_9H_{18}O$, which boils at 63° under 14 mm. pressure, has a sp. gr. 0·893 at 20°, and n_D 1·44862.

Diosphenol was obtained synthetically from hydroxymethylenementhone according to the stages (compare Martine, *Ann. Chim. Phys.*, 1904, [viii], 3, 49):



$$OH\cdot CH:C<\begin{matrix}CO-CHPr^{\beta}\\ CHMe\cdot CH_2\end{matrix}>CH_2 \longrightarrow CO<\begin{matrix}CO-CHPr^{\beta}\\ CHMe\cdot CH_2\end{matrix}>CH_2 \longrightarrow OH\cdot C<\begin{matrix}CO\cdot CHPr^{\beta}\\ CMe-CH_2\end{matrix}>CH_2.$$

Hydroxymethylenementhone is oxidised, best by ozone in presence of water, to the diketone, this undergoing change under the influence of acid into the enolic form, diosphenol. *Hydroxymethylenementhone* boils at 120° under 11 mm. pressure, has a sp. gr. 0·994 at 20°, n_D 1·49668, mol. refraction 53·6 (calc. for a keto-alcohol, 52·03, for a di-alcohol, 52·89).
W. A. D.

Carvone. II. Action of Magnesium Methyl Iodide on Carvone. HANS RUPE and KARL LIECHTENHAN (*Ber.*, 1906, 39, 1119—1126. Compare Abstr., 1905, i, 449).—The action of carvone on an ethereal solution of magnesium methyl iodide leads to the formation of a *hydrocarbon*, $C_{11}H_{16}$, which boils at 195—197° under 745·5 mm. pressure and at 72·5—74° under 9·5 mm., has a sp. gr. 0·8728, n_D 1·5007, $[\alpha]_D$ +70·38°, all at 20°, and forms only a tetrabromo-additive compound, although the molecular refraction requires the presence of three ethylenic linkings. The substance combines quantitatively with hydrogen ferricyanide and also with hydrogen ferrocyanide and hydrogen cobalticyanide, but in none of these cases can the pure hydrocarbon be regenerated. It is reduced by sodium and amyl alcohol to a *dihydro*-derivative, $C_{11}H_{18}$, which boils at 193—195° under 745 mm.

pressure, has a sp. gr. 0·8594, and $[\alpha]_D$ $-27·18°$ at 20°, and molecular refraction 50·11.

Methyldihydrocarvone, $C_{11}H_{18}O$, occurs as a by-product in the preparation of the hydrocarbon. It is separated in the form of the oxime, and, after purification by conversion into the semicarbazone, is obtained as a colourless oil which has the odour of dihydrocarvone, boils at 102—103·5° under 11 mm. pressure, and has a sp. gr. 0·9270 and n_D 1·48157 at 20°. Evidence is obtained which points to the possibility of the substance being a mixture of two isomerides. The *oxime*,

$$C_{11}H_{18}:NOH,$$

separates from dilute alcohol in glassy prisms and melts at 135—136°. The *semicarbazone*, $C_{12}H_{21}ON_3$, crystallises from methyl alcohol in hexagonal leaflets and melts at 180—181°.

8-Hydroxytetrahydrocarvone is obtained when dihydrocarvone is shaken with 40 per cent. sulphuric acid for twenty-four hours (compare Wallach, Abstr., 1893, i, 595; Baeyer, Abstr., 1894, i, 535). The *oxime*, $C_{10}H_{18}O:NOH$, obtained by the action of hydroxylamine hydrochloride in the presence of sodium hydrogen carbonate, is somewhat easily soluble in water; it separates from dilute alcohol in thick, glistening crystals and melts at 120—121°. The *semicarbazone*,

$$C_{11}H_{21}O_2N_3,$$

separates from methyl alcohol in large crystals and, when heated very slowly, softens at 150° and melts at 157—158° (compare Baeyer and Henrich, *Ber.*, 1895, **28**, 1590; Knoevenagel and Samel, Abstr., this vol., i, 296).

8-Hydroxytetrahydrocarvone, which by distillation with steam in the presence of 20 per cent. sulphuric acid is converted into carvenone, is reduced by sodium and alcohol to *α*-2 : 8-dihydroxyterpane (compare Abstr., 1905, i, 449). C. S.

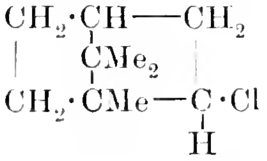
Pinene Hydrochloride and Camphene Hydrochloride. ALBERT HESSE (*Ber.*, 1906, **39**, 1127—1155).—The author discusses the evidence brought forward by Wagner and Bryckner (Abstr., 1900, i, 46) in support of their contention that pinene hydrochloride is bornyl chloride and camphene hydrochloride *iso*bornyl chloride, and points out its insufficiency; the facts given below, however, prove that Wagner's speculations in this direction were correct.

Attempts to bring about the interaction of pinene or camphene hydrochloride with magnesium according to Grignard's method, using the ordinary catalytic agents (iodine, aluminium chloride, alkyl haloids), were unsuccessful; but by adding the hydrochloride dissolved in benzene and ether to magnesium while the latter is acting vigorously on ethyl bromide dissolved in ether, a magnesium compound, $C_{10}H_{17}·MgCl$, is produced; in this case, magnesium ethyl bromide acts as a catalyst. With pinene hydrochloride, a yield of 80—85 per cent. of the magnesium compound is obtained, whilst 10—15 per cent. of the hydrochloride is converted into a d-*hydrodicamphene*, $(C_{10}H_{17})_2$, which crystallises from glacial acetic acid, melts at 85—87°, and has $[\alpha]_D$ $+28°42'$ in 20 per cent. benzene solution; small quantities of camphene and camphane are also formed. From camphene hydrochloride, 60 per cent. of the compound $C_{10}H_{17}·MgCl$ is produced, with about 20 per cent. of a *hydrodicamphene*, $C_{20}H_{34}$, which is perhaps identical with the *d*-hydrodicamphene formed from pinene hydrochloride; it melts, however, at 90—91°, has $[\alpha]_D$ + 2°37′, and may be a mixture.

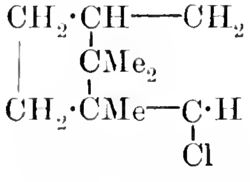
The same inactive camphane melting at 153° is obtained by decomposing with water the magnesium derivative of either active or inactive pinene hydrochloride or active or inactive camphene hydrochloride. On passing dry air or oxygen into the ethereal solution of the magnesium compound prepared from pinene hydrochloride and decomposing the product with dilute acid, a 65—85 per cent. yield of borneol is obtained; the remainder of the product consists principally of hydrodicamphene, with a small quantity of camphane and camphene; in some cases, 5—8 per cent. of *iso*borneol is obtained, formed partly from camphene hydrochloride present as an impurity in the pinene hydrochloride. From *l*-pinene hydrochloride ($[\alpha]_D$ – 26°3′), an *l*-borneol melting at 208—209° and having $[\alpha]_D$ – 11°6′ was obtained in one experiment; in another experiment, the *l*-borneol on crystallisation from light petroleum gave fractions with $[\alpha]_D$ varying from – 7° to – 3°. The rotatory power of the *l*-borneol thus obtained is therefore much smaller than that of natural *l*-borneol.

On oxidising the magnesium derivative of camphene hydrochloride in a similar manner, the product consists of about 30 per cent. of borneol, 15 per cent. of *iso*borneol, 21 per cent. of hydrodicamphene, and 34 per cent. of camphene and camphane. The production of so large a proportion of borneol is remarkable, and indicates either that in the preparation of the magnesium compound of camphene hydrochloride a considerable amount of the magnesium derivative of pinene hydrochloride is produced, or that during the oxidation of the magnesium compound isomeric change occurs.

Details are given of the methods used in determining the approximate composition of the various mixtures dealt with. The conclusions drawn from the data given above are (1) that pinene hydrochloride is bornyl chloride, and camphene hydrochloride *iso*bornyl chloride; (2) that these hydrochlorides are stereoisomeric, as shown in the formulæ:

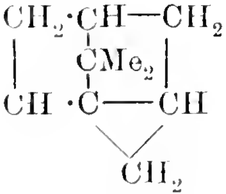


Pinene hydrochloride
(bornyl chloride).



Camphene hydrochloride
(*iso*bornyl chloride).

(3) that borneol and *iso*borneol are stereoisomeric secondary alcohols corresponding with the stereoisomeric chlorides; (4) that the formula of camphene is probably

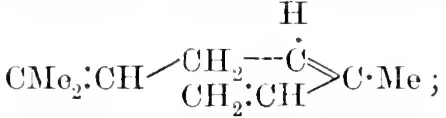


Camphene.

W. A. D.

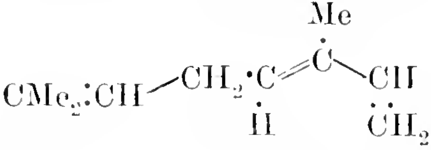
Ocimene and Myrcene. C. J. ENKLAAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, **8**, 714—723. Compare van Romburgh, Abstr., 1901, i, 220; Semmler, Abstr., 1901, i, 732; Chapman, Trans., 1903, **83**, 505).—Ocimene boils at 81° under 30 mm. pressure, or at 172·5° under atmospheric pressure, and has the sp. gr. 0·8031 at 15° and n_D 1·4857 at 18°. allo*Ocimene*, formed when ocimene is boiled under atmospheric pressure, boils at 81° under 12 mm. or at 188° under 750 mm. pressure, has the sp. gr. 0·8182 at 15° and n_D 1·5296, and absorbs oxygen and resinifies even more quickly than does ocimene. Ocimene and *allo*ocimene are stable at the ordinary temperature, although the latter polymerises when exposed to light. Myrcene polymerises slowly at the ordinary temperature. The end-point of the absorption of bromine by ocimene and by *allo*ocimene cannot be observed accurately, but the amount absorbed points to the presence of three ethylene linkings. On reduction with sodium and alcohol, myrcene, ocimene, and *allo*ocimene yield the same *dihydro-ocimene*, which boils at 166—168° under 761 mm. pressure, has the sp. gr. 0·7792 at 15° and n_D 1·4507 at 17°, and forms a *dibromide*; this separates from methyl alcohol in snow-white crystals and melts at 88°. In the presence of nickel at 180°, dihydro-ocimene absorbs hydrogen, forming a colourless liquid ($\beta\zeta$-dimethyloctane?), which boils at a much lower temperature than dihydro-ocimene.

The following formulæ are suggested: for ocimene,



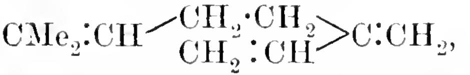
$$CMe_2{:}CH<\begin{matrix}CH_2\text{---}\overset{H}{\dot{C}}\\ CH_2{:}CH\end{matrix}>C{\cdot}Me;$$

for *allo*ocimene,



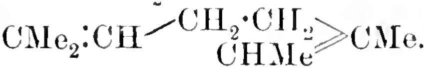
$$CMe_2{:}CH{-}CH_2{\cdot}\underset{H}{\dot{C}}{=}\overset{Me}{\dot{C}}{-}\underset{CH_2}{\overset{\cdot\cdot}{CH}};$$

and for myrcene,



$$CMe_2{:}CH<\begin{matrix}CH_2{\cdot}CH_2\\ CH_2{:}CH\end{matrix}>C{:}CH_2,$$

dihydro-ocimene having the constitution



$$CMe_2{:}CH<\begin{matrix}CH_2{\cdot}CH_2\\ CHMe\end{matrix}>CMe.$$

G. Y.

Aliphatic Terpene Alcohols. C. J. ENKLAAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, **8**, 723—727. Compare preceding abstract).—When digested with glacial acetic acid and dilute sulphuric acid at 50—60°, ocimene yields 10 per cent. of its weight of *ocimenol*, $C_{10}H_{18}O$, which boils at 97° under 10 mm. pressure, and has the sp. gr. 0·901 at 15° and n_D 1·4900 at 15°. It forms a *phenylurethane*, $C_{17}H_{23}O_2N$, which crystallises in white needles and melts at 72°.

Myrcenol (Barbier, Abstr., 1901, i, 477) is obtained from myrcene in a yield of about 20 per cent. of the theoretical; it forms a *phenylurethane*, $C_{17}H_{23}O_2N$, which melts at 68°.

The phenylurethane of linalool, prepared according to Wahlbaum and Hüthig's directions (Abstr., 1903, i, 506), is obtained in a yield of 85 per cent. of the theoretical if the process is prolonged for three months. The product consists of a mixture of the racemic with the optically active urethane, which melts at 66° and has a rotation of

23°27′ in a 200 mm. tube; from this the rotation of pure optically active linalool is calculated as 35°27′.

A mixture of the phenylurethanes of myrcenol and *r*-linalool melts at 60—62°. G. Y.

Sugar Components of the Glucosides Solanin, Convallamarin, and Scammonin.

Emil Votoček and Rudolf Vondráček (*Zeit. Zuckerind. Böhm.*, 1905, **30**, 117—120. Compare Abstr., 1905, i, 74).—On hydrolysis, both solanin and convallamarin yield *d*-galactose in addition to other sugars. Similarly, scammonin yields at least rhodeose and dextrose, so that the name scammonose represents a mixture and should not be used. T. H. P.

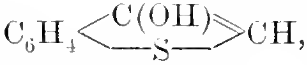
Sulphur Analogues of the Indigotin Group.

Paul Friedländer (*Ber.*, 1906, **39**, 1060—1066. Compare Friedländer and Mauthner, Abstr., 1905, i, 102).—o-*Carboxyphenylthioglycollic acid*, $CO_2H{\cdot}C_6H_4{\cdot}S{\cdot}CH_2{\cdot}CO_2H$, prepared from thiosalicylic acid, alkali, and chloroacetic acid, melts at 213°; its *monomethyl* ester,

$$CO_2Me{\cdot}C_6H_4{\cdot}S{\cdot}CH_2{\cdot}CO_2H,$$

melts at 151°, whilst its *dimethyl* ester melts at 52°. *o*-Carboxyphenylthioglycollic acid, when acted on by alkalis, forms *thioindoxylcarboxylic acid* [2-*hydroxythionaphthen*-1-*carboxylic acid*],

$$C_6H_4{<}\substack{C(OH)\\ S}{>}C{\cdot}CO_2H,$$

which readily loses carbon dioxide to form *thioindoxyl* [2-*hydroxythionaphthen*],  $C_6H_4{<}\substack{C(OH)\\ S}{>}CH$, which crystallises in needles, melts at 71°, and readily assumes a red tint on exposure to the atmosphere. On the addition of potassium ferricyanide to its solution in sodium hydroxide, the *dye*, $C_{16}H_8O_2S_2$, separates in red flakes. It is assumed that the latter substance has a structure analogous with that of indigotin. It crystallises from xylene in needles with a bronze lustre; its solution in chloroform is fluorescent; at a high temperature, it is more stable than indigotin; it sublimes in needles, and in small amounts can be distilled without undergoing decomposition; it is very stable towards oxidising agents.

Thioindoxyl is also analogous to indoxyl; it is readily oxidised to a dye; it readily combines with aromatic aldehydes, ketones, and diketones to form thioindogenides.

Thioindoxylcarboxylic acid, like indoxylcarboxylic acid, readily loses carbon dioxide, and is characterised by the difficulty with which its ester is saponified.

The preparation of various other compounds is indicated, details of which are promised in a subsequent paper. A. McK.

Alkaloids of Anagyris fœtida.

G. Goessmann (*Arch. Pharm.*, 1906, **244**, 20—24. Compare Schmidt, Litterscheid, and Klostermann, Abstr., 1900, i, 513).—The crude alkaloids were prepared from the seeds by the method of Partheil and Spasski (Abstr., 1896, i, 657). They were converted into phenylthiocarbamides by allowing them to remain in alcoholic solution with phenylthiocarbimide. The solid cytisine derivative was filtered off, and from the filtrate (by evaporation, heating of the residue with dilute hydrochloric acid, and further treatment) an alkaloid, or mixture of alkaloids, "anagyrine," was obtained; this is resinous, boils at 245° under 30 mm. pressure, and contains C 72·4, H 8·68, N 11·68 per cent., which does not accord well with the formula $C_{15}H_{22}ON_2$; it forms 65 per cent. of the crude alkaloids.

The cytisine can be regenerated from its phenylthiocarbamide by heating the latter with concentrated hydrochloric acid at 150°.

C. F. B.

Cocaine Formate. FERD. VIGIER (*J. Pharm. Chim.*, 1906, [vi], **23**, 97—98).—This salt, prepared by adding formic acid (1 mol.) to cocaine (1 mol.) suspended in water, crystallises from water in colourless, silky needles, melts at about 42°, dissolves in 41 parts of water and in 2·3 parts of alcohol at 20°, and has $[\alpha]_D - 56°40'$ in water at the same temperature. The salt possesses a slightly bitter taste: it is hydrolysed by water at 90°.

T. A. H.

Alkaloids from Species of Datura which induce Mydriasis. ERNST SCHMIDT (*Arch. Pharm.*, 1906, **244**, 66—71. Compare Abstr., 1905, i, 717).—The seeds of a variety of *Datura fastuosa*, designated *flor. cœrul. plen.*, were found to contain 0·22 per cent. scopolamine and 0·034 hyoscyamine, whilst those of a variety designated *flor. alb. plen.* contained 0·20 and 0·023 per cent. respectively, a little atropine being present in both cases. *D. fastuosa* is thus certainly not identical with *D. alba* (Shimoyama and Koshima, *Apoth. Zeit.*, 1892, 458).

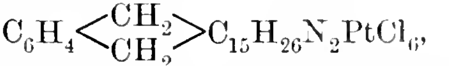
[With ADOLF KIRCHER.]—In the seeds of *D. arborea*, procured from abroad, scopolamine and hyoscyamine were found in the proportion 1 : 4. The other parts of a plant grown in Marburg, several years old and in flower when gathered, had been found to contain mainly scopolamine (*loc. cit.*). The stem of a younger plant, however, grown in Marburg and gathered after it had flowered, contained mainly hyoscyamine; yet the root of this plant contained but little hyoscyamine.

C. F. B.

Sparteine Alkylhaloids. MAX SCHOLTZ (*Arch. Pharm.*, 1906, **244**, 72—77. Compare Abstr., 1904, i, 1045).—The statement made previously, that different compounds are obtained by the successive addition to sparteine of two different alkylhaloids in different order, is erroneous.

Sparteine forms a *benzyl iodide*, $C_{15}H_{26}N_2,CH_2PhI$, melting at 168°, by simple addition at the ordinary temperature.

A quaternary *platinichloride*,



$C_6H_4{<}{}^{CH_2}_{CH_2}{>}C_{15}H_{26}N_2PtCl_6$,

melting and decomposing at 218°, can be obtained from the additive product of sparteine with *o*-xylylene bromide, and another, $C_{15}H_{26}N_2Me_2PtCl_6$, from the additive compound obtained by heating sparteine with excess of methyl iodide at 180—190°.

C. F. B.

Hydroxybenzylpiperidines and Dibromo-*p*-hydroxy-ψ-cumylanilines. KARL AUWERS and A. DOMBROWSKI (*Annalen*, 1906, **344**, 280—299. Compare Hildebrandt, Abstr., 1900, ii, 676; 1905, i, 80).—Hydroxybenzylpiperidines are formed by the simultaneous action of formaldehyde and secondary amines on phenols, which contain either an *o*- or a *p*-hydrogen atom, in aqueous-alcoholic solution. The following new substances, $C_5NH_{10}\cdot CH_2R$, are described.

From *m*-cresol, R = p-*hydroxy*-o-*methylphenyl*: large, glistening prisms, melts at 57°, and is moderately soluble in water. From *v*-*o*-xylenol, R = 4-*hydroxy*-2 : 3-*dimethylphenyl*: an oil, which forms a crystalline hydrochloride. From *v*-*m*-xylenol, R = 4-*hydroxy*-3 : 5-*dimethylphenyl*: stout needles, melts at 117·5—118·5°, and is slightly soluble in water. From *s*-*m*-xylenol, R = 4-*hydroxy*-2 : 6-*dimethylphenyl*: large, transparent needles, melts at 98·5°, and is only sparingly soluble in water. From *p*-xylenol, R = 4-*hydroxy*-2 : 5-*dimethylphenyl*: slender, white needles, melts at 131·5—132°, and is almost insoluble in water. From ψ-cumenol, R = 2-*hydroxy*-3 : 5 : 6-*trimethylphenyl*: nacreous scales or large, hexagonal plates, melts at 69—70°, and is almost insoluble in water. From guaiacol, R = 3-*methoxy*-4-*hydroxyphenyl*: stout needles, melts at 99·5—100·5°. From *o*-nitrophenol, R = 3-*nitro*-4-*hydroxyphenyl*: iridescent, red needles, melts at 140—141·5°, and is sparingly soluble in water.

The hydroxybenzylpiperidines are almost all soluble in the usual organic solvents except in petroleum, only the derivatives of thymol, carvacrol, and the naphthols are less readily soluble. Those which are more or less soluble in water are correspondingly volatile in a current of steam.

The substance  $C_6H_4\left<\begin{matrix}C(CH_2\cdot NMe_2)\\ CH{=\!=\!=}CH\end{matrix}\right>C\cdot OH$, formed by the action of dimethylamine and formaldehyde on β-naphthol, crystallises in small leaflets and melts at 74—75°.

The following derivatives of dibromo-*p*-hydroxy-ψ-cumylaniline (Auwers and Marwedel, Abstr., 1896, i, 149),

$$OH\cdot C\left<\begin{matrix}CMe\cdot CBr\\ CBr{:}CMe\end{matrix}\right>C\cdot CH_2\cdot NHR,$$

are formed by the action of dibromo-*p*-hydroxy-ψ-cumyl bromide on the base in ethereal solution.

From *o*-toluidine, $R = C_6H_4Me$: white, fine crystalline powder, m. p. 154—154·5°. From *m*-toluidine, $R = C_7H_7$: white, crystalline powder, m. p. 123·5—125°. From *p*-toluidine, $R = C_7H_7$: small, stout prisms, m. p. 96—98°. From *as*-*o*-xylidine, $R = C_6H_3Me_2$: slightly yellow powder, m. p. 120°. From *v*-*o*-xylidine, $R = C_6H_3Me_2$: slightly red, fine crystalline powder, m. p. 158°. From *as*-*m*-xylidine, $R = C_6H_3Me_2$: slender needles, m. p. 144·5—145·5°. From *v*-*m*-xylidine, $R = C_6H_3Me_2$: white, crystalline powder, m. p. 144·5—146°; is formed together with the *dicumyl* derivative,

$$C_6H_3Me_2\cdot N(CH_2\cdot C_6Me_2Br_2\cdot OH)_2,$$

which is obtained as a white, sparingly soluble, crystalline powder melting at 207—208°. From *s*-*m*-xylidine, $R = C_6H_3Me_2$: slender needles, m. p. 153·5—155°; is formed together with

$$C_6H_3Me_2\cdot N(CH_2\cdot C_6Me_2Br_2\cdot OH)_2,$$

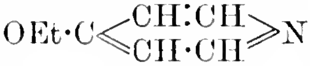
melting at 213—214°. From *p*-xylidine, $R = C_6H_3Me_2$: slender needles, melts at 155·5—157°. From *ψ*-cumidine, $R = C_6H_2Me_3$: small, glistening needles and prisms, m. p. 140—141·5°. G. Y.

Physical Constants of Pure Pyridine.

JAN VON ZAWIDZKI (*Chem. Zeit.*, 1906, **25**, 299).—Two samples of pyridine, purified by repeated fractional distillation and drying with solid sodium hydroxide, were found to solidify at 42°. Altschul and Schneider (Abstr., 1895, ii, 206) state that pyridine does not solidify when cooled to − 200°. The two samples gave the following values: boiling point, 115·1° and 115·3° under normal pressure; sp. gr. 0·97794 and 0·97796 at 25°/4°, and n_D 1·50700 and 1·50729 at 25°. P. H.

Etherification of 4-Pyridones with Diazo-derivatives of Aliphatic Hydrocarbons.

ALBERTO PERATONER and E. AZZARELLO (*Atti R. Accad. Lincei*, 1906, [v], **15**, i, 139—144).—When 4-pyridone is etherified by means of diazomethane or diazoethane, the alkyl residue enters both the NH-group and also the hydroxy-group of the tautomeric hydroxypyridine. This affords an exception to von Pechmann's rule, which states that, with tautomeric substances, the methyl derivative obtained is mainly that corresponding with the form possessing the most marked acid character.

4-*Ethoxypyridine*,  $OEt\cdot C{<}\begin{matrix}CH{:}CH\\CH\cdot CH\end{matrix}{>}N$, is a colourless liquid which has an odour resembling that of pyridine, boils at 96° under 15 mm. pressure, and is miscible with alcohol. T. H. P.

Action of Formaldehyde on *α*-Picoline (2-Methylpyridine).

ANDREAS LIPP and E. ZIRNGIBL (*Ber.*, 1906, **39**, 1045—1054. Compare Lipp and Richard, Abstr., 1904, i, 342).—*Trimethylol-2-picoline*, $C_5NH_4\cdot C(CH_2\cdot OH)_3$, is formed, together with the corresponding mono- and di-methylol compounds, when 2-picoline is heated with 40 per cent. formaldehyde for twenty-seven hours at 135—140°. Better yields may be obtained by heating the dimethylol compound in a similar manner. It is most readily separated from the dimethylol compound by means of the mercurichloride, which is more readily soluble in water than the corresponding salt of dimethylol-2-picoline.

Trimethylol-2-picoline crystallises from chloroform or dry ether in colourless needles, melts at 68°, and begins to decompose at 170°. It dissolves readily in water to an alkaline solution. The *hydrochloride* has been obtained as an oil only; the *mercurichloride*,

$$C_9H_{13}O_3N,HCl,6HgCl_2,$$

crystallises from hot water in colourless, glistening prisms, melting at 138° and readily soluble in cold alcohol; the *platinichloride* crystallises in quadratic plates, decomposes at 167—168°, and is insoluble in absolute alcohol; the *aurichloride* forms yellow prisms melting at 140°, and the *picrate* yellow prisms melting at 111·5—112·5°, and only sparingly soluble in cold water. *Trimethylol-2-picoline methochloride* is an oil and is readily soluble in water or alcohol. It yields a *mercurichloride*, $C_{10}H_{16}O_3NCl,6HgCl_2$, which crystallises in short, glistening prisms melting at 152—153°; a *platinichloride* crystallising in needles and decomposing at 151°, and an *aurichloride* melting at 138—140°.

Trimethylol-2-picoline tribenzoate, $C_5NH_4\cdot C(CH_2\cdot OBz)_3$, crystallises from methyl alcohol in needles melting at 94°, and yields a *platinichloride*, $C_{60}H_{50}O_{12}N_2,H_2PtCl_6,2\frac{1}{2}H_2O$, in the form of glistening needles which decompose at 182°. The *triacetate*, $C_5NH_4\cdot C(CH_2\cdot OAc)_3$, forms a thick oil, only sparingly soluble in water and of neutral reaction. The corresponding *platinichloride* melts at 159°.

When dimethylol-2-picoline is distilled in a current of steam, a volatile *base*, $C_5NH_4\cdot CH\left<\begin{matrix}CH_2\\CH_2\end{matrix}\right>O$, passes over. It is a colourless oil distilling at 130—134° under 11 mm. pressure, has an odour of tobacco juice, dissolves sparingly in water, and the solution has an alkaline reaction. The *hydrochloride* crystallises from alcohol and is extremely hygroscopic; the *mercurichloride*, $C_8H_9ON,HCl,6HgCl_2$, forms glistening prisms, melts at 171—172°, and is very sparingly soluble in cold water; the *platinichloride* forms glistening, orange-red prisms, begins to decompose at 168°, and is readily soluble in hot water; the *aurichloride* crystallises in golden-yellow plates melting at 112·5—113·5°, and the *picrate* crystallises in yellow prisms melting at 109°. When boiled with hydrochloric acid, the anhydro-base is decomposed according to the equation

$$C_5NH_4\cdot CH{:}C_2H_4O + H_2O = CH_2O + C_5NH_4\cdot CH_2\cdot CH_2\cdot OH,$$

and monomethylol-2-picoline is formed. J. J. S.

5-Bromo-6-aminoquinoline. WILHELM MEIGEN (*J. pr. Chem.*, 1906, [ii], **73**, 248—253. Compare this vol., i, 319).—The product obtained on brominating 6-aminoquinoline in glacial acetic acid is 5-bromo-6-aminoquinoline and not 7-bromo-6-aminoquinoline, as supposed by Claus and Schnell (Abstr., 1896, i, 319), as it is obtained on reduction with iron and acetic acid of 5-bromo-6-nitroquinoline, which melts at 126° and is formed together with 5-bromo-8-nitroquinoline, melting at 146°, on nitration of 5-bromoquinoline.

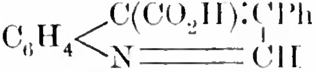
5-Bromo-6-aminoquinoline crystallises in characteristic, silvery leaflets containing $2H_2O$, and melts at 83°, or, when anhydrous, at 127°. When diazotised and reduced with stannous chloride in hydrochloric acid solution, and the resulting tin salt boiled with sodium acetate and copper sulphate, 5-bromo-6-aminoquinoline yields a product which melts at 48° and is probably 5-bromoquinoline, containing small quantities of 5-chloroquinoline. On nitration, this yields a product melting at 136° which, when reduced, diazotised, and boiled with cuprous bromide, yields 5 : 8-dibromoquinoline.

5 : 6-Dibromoquinoline, obtained from 5-bromo-6-aminoquinoline, melts at 80—81°; it is formed also from 6-bromoquinoline by nitration and reduction and boiling the product with cuprous bromide. It forms a crystalline *platinichloride*; the *methiodide* crystallises in slender, yellow needles and melts at 250°.

5 : 6-*Dibromo*-8-*nitroquinoline*, formed from 5 : 6-dibromoquinoline, crystallises in yellow needles and melts at 196°.

The constitution of Claus' dibromoquinoline, melting at 135° (Abstr., 1896, i, 254), remains to be determined. G. Y.

3-Phenylcinchonic Acid. H. Hübner (*Ber.*, 1906, **39**, 983—985).—*Potassium 3-phenylcinchonate* is prepared by heating 2 mols. of isatin and 1 mol. of phenylacetaldoxime in an excess of concentrated aqueous potassium hydroxide on the water-bath for twelve hours. The *acid*,



$$C_6H_4<\begin{array}{l}C(CO_2H):CPh\\ N=\!=\!=\!=\!=CH\end{array}$$

crystallises in microscopic cubes or short prisms, melts at 273°, is sparingly soluble in glacial acetic acid or acetone, and is almost insoluble in other organic solvents. The *sodium* salt forms glistening crystals; the *silver* salt, $C_{16}H_{10}O_2NAg$, was analysed; the *sulphate* forms long, transparent needles; the *chromate*, $(C_{16}H_{11}O_2N)_2CrO_3$, is obtained as a dark yellow powder. When treated with thionyl chloride, the acid forms a sparingly soluble, crystalline product, which is probably the *hydrochloride* of the acid chloride; this reacts with methyl alcohol, ammonia, aniline, or hydrazine to form the following substances: the *methyl* ester, $C_9NH_5Ph{\cdot}CO_2Me$, crystallises in white needles and melts at 73°; the *amide*, $C_9NH_5Ph{\cdot}CO{\cdot}NH_2$, forms a microcrystalline powder and melts at 274°; the *anilide*, $C_{22}H_{16}ON_2$, crystallises in needles and melts at 222°; the *hydrazide*, $C_{16}H_{13}ON_3,H_2O$, crystallises in long, hexagonal plates and melts at 154°. G. Y.

Derivatives of 5-Phenylacridine. I. Albert E. Dunstan and Robert O'F. Oakley (*Ber.*, 1906, **39**, 977—980).—The *chromate* of 5-phenylacridine (Bernthsen, Abstr., 1883, 580), $(C_{19}H_{13}N)_2H_2CrO_4$, forms a voluminous, yellow precipitate.

2 : 8-*Diamino-5-phenylacridine*, $C_{19}H_{15}N_3$, obtained by reducing 2 : 8-dinitro-5-phenylacridine (Bernthsen, *Ber.*, 1884, 1356) with stannous chloride in alcoholic hydrochloric acid, crystallises in nodular aggregates, and is darker coloured than chrysaniline. The *picrate*, $C_{19}H_{15}N_3(C_6H_3O_7N_3)_3$, the *platinichloride*, $C_{19}H_{15}N_3,H_2PtCl_6$, and the *dichromate*, $(C_{19}H_{15}N_3)_2,H_2Cr_2O_7$, were analysed; the *diacetyl* derivative is orange-yellow, and forms a *methiodide* which dissolves in methyl alcohol to a red solution. G. Y.

Derivatives of 5-Phenylacridine. II. Halogen Derivatives of the Acridine Group. Albert E. Dunstan and Robert O'F. Oakley (*Ber.*, 1906, **39**, 981—982).—Bromination of 5-phenylacridine leads to the formation of a *monobromo*-derivative, $C_{19}H_{12}NBr$, which crystallises in yellow needles, has no constant melting point, and does not form fluorescent solutions; with an excess of bromine in presence of iodine, a *tribromo*-derivative, $C_{19}H_{10}NBr_3$, crystallising in brown needles, is formed.

The action of chlorine on 5-phenylacridine in chloroform solution leads to the formation of a fluorescent, yellow solution which slowly deposits the *dichloro*-derivative, $C_{19}H_{11}NCl_2$, in needles; this is obtained also as a yellow, voluminous precipitate when 5-phenylacridine is chlorinated with bleaching powder. G. Y.

Products of the Condensation of Rhodanic Acid with Aldehydes. Guido Bargellini (*Atti R. Accad. Lincei*, 1906, [v], **15**, i, 35—43. Compare Zipser, Abstr., 1903, i, 273, and Andreasch and Zipser, Abstr., 1903, i, 855).—The condensation products described by the author were prepared by heating rhodanic acid and an aldehyde in alcoholic solution with sulphuric or hydrochloric acid.

The salicylidene compound melts and decomposes at 218—219°; Zipser (*loc. cit.*) gave 200° as the melting point.

m-*Hydroxybenzylidenerhodanic acid*,  $OH\cdot C_6H_4\cdot CH{:}C<\begin{matrix}S-CS\\ \quad\;|\\ CO\cdot NH\end{matrix}$, crystallises from aqueous alcohol in greenish-yellow needles melting at 244—245° and dissolves readily in alcohol, acetic acid, ethyl acetate, or acetone, and to a slight extent in benzene or chloroform.

p-*Hydroxybenzylidenerhodanic acid*, $C_{10}H_7O_2NS_2$, crystallises from aqueous alcohol in reddish-yellow needles which begin to melt and decompose at 260° and dissolves readily in ethyl or amyl alcohol, acetic acid, ethyl acetate, ether, or acetone, and to a less extent in benzene or chloroform.

2-*Hydroxy*-5-*methylbenzylidenerhodanic acid*,

$$OH\cdot C_6H_3Me\cdot CH{:}C<\begin{matrix}S-CS\\ \quad\;|\\ CO\cdot NH\end{matrix},$$

prepared from rhodanic acid and *p*-homosalicylaldehyde, crystallises from aqueous alcohol in litharge-yellow needles melting and decomposing at 217—218°, and dissolves readily in alcohol, acetic acid, ethyl acetate, ether, or acetone, and moderately so in benzene or chloroform.

4-*Hydroxy*-3-*methoxybenzylidenerhodanic acid*, $C_{11}H_9O_3NS_2$, prepared from rhodanic acid and vanillin, crystallises from acetic acid in lemon-yellow needles melting at 227—230°, and dissolves moderately well in alcohol, ethyl acetate, or acetone, and sparingly in ether, benzene, or chloroform.

3 : 4-Methylenedioxybenzylidenerhodanic acid begins to turn brown at 256°, and at 258° is converted into a semi-fused, black mass (compare Andreasch and Zipser, *loc. cit.*).

Cinnamylidenerhodanic acid melts at 220—221°; according to Zipser (*loc. cit.*), it melts and decomposes at 208—211°. By the action of bromine in chloroform solution it is converted into a yellowish-white *compound* melting and decomposing at about 160°.

Furfurylidenerhodanic acid,  $\begin{matrix}CH-O\\ \|\\ CH\cdot CH\end{matrix}>C\cdot CH{:}C<\begin{matrix}S-CS\\ \quad\;|\\ CO\cdot NH\end{matrix}$, crystallises from alcohol in yellowish-orange needles, commencing to melt and decompose at 220°, and completely changing to a black liquid at 230°; it dissolves readily in acetic acid, acetone, ether, or chloroform, and sparingly in benzene. T. H. P.

Action of Grignard's Reagents on Michler's Ketone. MARTIN FREUND and FRITZ MAYER (*Ber.*, 1906, 39, 1117—1119. Compare Klages, Abstr., 1902, i, 666).—The action of magnesium methyl iodide on Michler's ketone leads to the formation of *tetramethyldiaminodiphenylethylene*, $CH_2{:}C(C_6H_4\cdot NMe_2)_2$, which crystallises in glistening leaflets, melts at 115—117°, and is reduced by red phosphorus and hydriodic acid to tetramethyldiaminodiphenylethane. *Tetramethyldiaminodiphenylpropylene*, $CHMe{:}C(C_6H_4\cdot NMe_2)_2$, forms small, greenish-yellow needles, melts at 99—100°, and is reduced to *tetramethyldiamino-*

diphenylpropane, $CH_2Me\cdot CH(C_6H_4\cdot NMe_2)_2$, which crystallises in white needles and melts at 50—51°. C. S.

Action of Secondary Asymmetric Hydrazines on Sugar. III.

RUDOLF OFNER (*Monatsh.*, 1906, **27**, 75—80. Compare Abstr., 1905, i, 158, 937).—The *osazone*, $C_{22}H_{30}O_4N_4$, is formed in a few minutes by the action of *as*-phenylethylhydrazine on lævulose in alcohol acetic acid solution, or is obtained in a yield of 55—60 per cent. of the theoretical when dextrose is digested with the hydrazine in alcohol acetic acid solution in a closed vessel for twenty hours at the laboratory temperature; it crystallises from ethyl acetate in slender, lemon-yellow needles and melts at 143°.

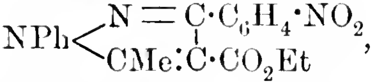
The *phenylethylhydrazone*, $C_{14}H_{22}O_5N_2$, formed by the action of *as*-phenylethylhydrazine on dextrose in boiling alcoholic solution, crystallises from ethyl alcohol in slender, white needles, which contain C_2H_6O, sinter at 80°, and melt at 116—118°, or from methyl alcohol in small plates which contain $\frac{1}{2}CH_4O$ and melt at 112—116°.

G. Y.

Pyrazole Derivatives.

GAETANO MINUNNI and GUIDO LAZZARINI (*Atti R. Accad. Lincei*, 1906, [v], **15**, i, 19—24. Compare Abstr., this vol., i, 114).—Ethyl 1 : 3-diphenyl-5-methylpyrazole-4-carboxylate, already obtained by Knorr and Blank (Abstr., 1885, 810), may be more readily prepared by the action of ethyl acetoacetate on benzaldehydephenylhydrazone.

Ethyl 1-*phenyl*-3-m-*nitrophenyl*-5-*methylpyrazole*-4-*carboxylate*,



$$NPh<\begin{matrix}N=C\cdot C_6H_4\cdot NO_2\\ \ \ \ \ \ \ \ |\\ CMe:C\cdot CO_2Et\end{matrix},$$

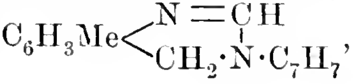
prepared by the condensation of *m*-nitrobenzaldehydephenylhydrazone with ethyl acetoacetate in presence of zinc chloride, crystallises from alcohol in slender, colourless needles melting at 105·5—106·5° and is sparingly soluble in light petroleum, more readily in ether or amyl alcohol, and very readily in benzene, ethyl acetate, or chloroform. The free *acid*, $C_{17}H_{13}O_4N_3$, crystallises from benzene with $\frac{1}{2}C_6H_6$ in rosettes of slender, white needles melting and decomposing at 207—208° and dissolves in alcohol or chloroform and, to a slight extent, in ether.

Ethyl 1-*phenyl*-3-p-*nitrophenyl*-5-*methylpyrazole*-4-*carboxylate*,

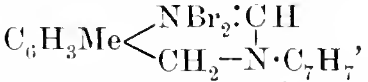
$$C_{19}H_{17}O_4N_3,$$

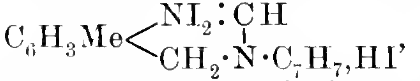
prepared from *p*-nitrobenzaldehydophenylhydrazone and ethyl acetoacetate, crystallises from alcohol in small, yellow needles melting at 107—108° and dissolves sparingly in ether and readily in acetone or chloroform. The corresponding *acid*, $C_{17}H_{13}O_4N_3$, crystallises from benzene with $\frac{1}{2}C_6H_6$ in tufts of slender, white needles melting and decomposing at 209·5—210° and dissolves slightly in ether and readily in alcohol or acetone. T. H. P.

Quinazolines from *o*-Amino-*m*-xylyl-*p*-toluidine.

REINHOLD VON WALTHER and R. BAMBERG (*J. pr. Chem.*, 1906, [ii], 73, 209—228. Compare Abstr., 1905, i, 298).—3-p-*Tolyl*-6-*methyl*-3 : 4-*dihydroquinazoline*,  $C_6H_3Me<\begin{matrix}N=CH\\ \ \ \ \ \ \ |\\ CH_2\cdot N\cdot C_7H_7\end{matrix}$, is obtained by boiling *o*-amino-*m*-xylyl-

p-toluidine with ethyl *o*-formate, or with 80 per cent. formic acid, in a reflux apparatus; it crystallises in white, hexagonal leaflets, melts at 158°, and is readily soluble in benzene, chloroform, alcohol, or ether. The *hydrochloride*, $C_{16}H_{16}N_2,HCl,3H_2O$, crystallises in white needles, loses $3H_2O$ at 130°, and, when anhydrous, melts at 212°; the *nitrate* crystallises in long, slightly yellow needles, melts at 95°, and is decomposed at 170°; the picrate, $C_{22}H_{19}O_7N_5$, forms orange-yellow needles and melts at 201°; the *platinichloride*, $(C_{16}H_{16}N_2)_2,H_2PtCl_6$, crystallises in sheaves of yellow needles and melts at 202°.

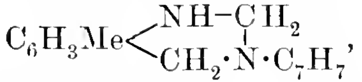
With bromine in absolute alcoholic solution, the base forms the *additive* compound,  $C_6H_3Me<\begin{matrix}NBr_2:CH \\ CH_2-N\cdot C_7H_7\end{matrix}$, which crystallises in red needles, and from which the base is re-formed on successive treatment with sulphur dioxide and potassium hydroxide in alcoholic solution. With iodine in alcoholic solution, the base yields the *product*



$$C_6H_3Me<\begin{matrix}NI_2:CH \\ CH_2\cdot N\cdot C_7H_7,HI\end{matrix}$$

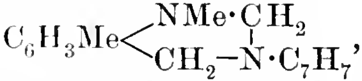
which forms red crystals having a metallic lustre, and decomposed by sulphur dioxide in alcoholic solution.

3-p-*Tolyl*-6-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinazoline*,



$$C_6H_3Me<\begin{matrix}NH-CH_2 \\ CH_2\cdot N\cdot C_7H_7\end{matrix}$$

is prepared by reducing the dihydro-base with absolute alcohol and sodium; it crystallises in white needles, melts at 138°, and is readily soluble in benzene or chloroform, but only moderately so in alcohol or ether. The *hydrochloride* crystallises in white cubes, the *nitrate* in long, yellow needles, and the *sulphate* in small, white needles; the *platinichloride*, $(C_{16}H_{18}N_2)_2,H_2PtCl_6$, separates from glacial acetic acid in stout, yellow needles, or from alcohol in microscopic, brown crystals, and melts at 203—205°; the *picrate*, $C_{22}H_{21}O_7N_5$, crystallises in orange-yellow needles, becomes red on exposure to air, and melts at 200°.

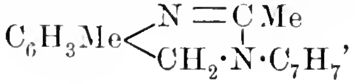
The action of methyl iodide and methyl alcohol on the tetrahydro-base in a sealed tube at 100° leads to the formation of 3-p-*tolyl*-1 : 6-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinazoline*,  $C_6H_3Me<\begin{matrix}NMe\cdot CH_2 \\ CH_2-N\cdot C_7H_7\end{matrix}$, which crystallises in rhombic plates and melts at 155°. The *hydrochloride* forms quadratic plates, and the *platinichloride* sheaves of crystals.

o-*Acetylamino*-m-*xylyl*-p-*acetotoluidide*,

$$NHAc\cdot C_6H_3Me\cdot CH_2\cdot NAc\cdot C_6H_3Me,$$

formed by heating *o*-amino-*m*-xylyl-*p*-toluidine with acetic anhydride on the water-bath, crystallises in hexagonal leaflets, melts at 135°, and when boiled with dilute hydrochloric or sulphuric acid, or heated with dilute hydrochloric acid under pressure at 160°, is hydrolysed with formation of the base.

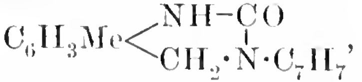
3-p-*Tolyl*-2 : 6-*dimethyl*-3 : 4-*dihydroquinazoline*,



$$C_6H_3Me<\begin{matrix}N=CMe \\ CH_2\cdot N\cdot C_7H_7\end{matrix},$$

is formed when *o*-amino-*m*-xylyl-*p*-toluidine is heated with acetiminoether in benzene solution; it crystallises from light petroleum in nodular aggregates of large, stout crystals and melts at 89—93°. The *hydrochloride* crystallises in transparent, quadratic leaflets and melts at 261°; the *platinichloride* forms sheaves of orange-yellow needles melting at 235°, or quadratic leaflets melting and decomposing at 207°.

2-*Keto*-3-p-*tolyl*-6-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinazoline*,



$$C_6H_3Me<\begin{array}{l}NH-CO\\CH_2\cdot N\cdot C_7H_7\end{array},$$

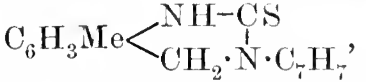
is obtained (1) by heating *o*-amino-*m*-xylyl-*p*-toluidine with carbamide at about 150°, or (2) by passing carbonyl chloride into a solution of the *p*-toluidine derivative in benzene; it crystallises in white needles, melts at 238—240°, and is readily soluble in hot alcohol, ethyl acetate, or benzene.

The *dicarbamide* derivative,

$$NH_2\cdot CO\cdot NH\cdot C_6H_3Me\cdot CH_2\cdot N(C_7H_7)\cdot CO\cdot NH_2,$$

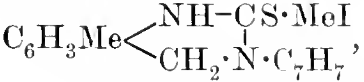
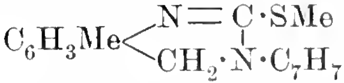
formed by the action of potassium cyanate on *o*-amino-*m*-xylyl-*p*-toluidine in hydrochloric acid solution, is obtained as a white, crystalline powder and melts and decomposes forming the keto-tetrahydroquinazoline at 219°.

2-*Thion*-3-p-*tolyl*-6-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinazoline*,



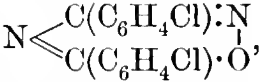
$$C_6H_3Me<\begin{array}{l}NH-CS\\CH_2\cdot N\cdot C_7H_7\end{array},$$

prepared by heating *o*-amino-*m*-xylyl-*p*-toluidine with carbon disulphide and flowers of sulphur in absolute alcohol in a sealed tube at 130—160°, is obtained in a yield of 83 per cent. of the theoretical; it crystallises in transparent, hexagonal leaflets, becomes yellow at 200°, melts at 258—260°, and forms sparingly soluble salts. When reduced with sodium and alcohol, it yields the tetrahydro-base melting at 138°. The *sulphate* forms small, twisted needles and does not melt at 275°; the *hydrochloride* crystallises in leaflets and melts at 220—225°; the *platinichloride* forms microscopic, orange-yellow crystals, and melts and decomposes at 250°; the *picrate* forms transparent, hexagonal, yellow plates and melts at 240°; the *acetate* crystallises in hexagonal plates and melts at 257°; the *oxalate* crystallises in long, white needles and melts at 247—252°.

When heated with methyl iodide and methyl alcohol in a sealed tube at 130°, the thiontetrahydroquinazoline yields the *additive* compound,  $C_6H_3Me<\begin{array}{l}NH-CS\cdot MeI\\CH_2\cdot N\cdot C_7H_7\end{array}$, which crystallises in yellow prisms, commences to become brown at 255°, melts and decomposes at 260°, and when heated with 70 per cent. alcohol forms 2-*methylthiol*-3-p-*tolyl*-6-*methyl*-3 : 4-*dihydroquinazoline*,  $C_6H_3Me<\begin{array}{l}N=C\cdot SMe\\CH_2\cdot N\cdot C_7H_7\end{array}$. This crystallises in delicate, white leaflets, or small, transparent prisms and melts at 87°; the *sulphate* forms long, slender, white needles and melts at 208°; the *hydrochloride* forms short spears and melts at 258°; the *platinichloride* forms microscopic, stout crystals and melts at 222°; the *picrate* forms slender, yellow needles and melts at 168°. When reduced with zinc dust and dilute sulphuric acid, the methylthiol base yields 3-*p*-tolyl-6-methyl-1 : 2 : 3 : 4-tetrahydroquinazoline, melting at 138°. G. Y.

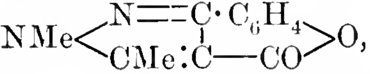
Action of Amyl Nitrite on Oximes. HARTWIG FRANZEN and F. ZIMMERMANN (*J. pr. Chem.*, 1906, [ii], **73**, 253—256. Compare Minunni and Ciusa, this vol., i, 187).—The action of amyl nitrite on benzaldoxime in ethereal or benzene solution leads to the formation, (1) when cooled by ice, of benzaldoxime peroxide, which melts at 105°, together with benzaldehyde and benzoic acid, or, (2) when heated, of dibenzenylazoxime, which melts at 108°.

The following substances are formed from the corresponding aldoximes in the same way.

m-Nitrobenzaldoxime peroxide melts at 124°; di-*m*-nitrobenzenylazoxime melts at 184°; *di*-m-*chlorobenzenylazoxime*,  $N\!\!<\!\begin{array}{l}C(C_6H_4Cl){:}N\\ C(C_6H_4Cl){\cdot}O\end{array}$, separates from benzene as a white precipitate and melts at 115°; p-*methoxybenzaldoxime peroxide*, $O_2(N{:}CH{\cdot}C_6H_4{\cdot}OMe)_2$, crystallises in glistening, brown leaflets and melts at 119·5°.

The action of ethyl nitrite on benzaldoxime and *p*-methoxybenzaldoxime in ethereal solution leads to the formation of benzaldoxime and *p*-methoxybenzaldoxime peroxides respectively. G. Y.

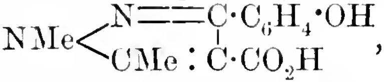
1-Phenyl-3-hydroxyphenyl-5-methylpyrazole-4-carboxylic Acid and its Lactone. GAETANO MINUNNI and G. LAZZARINI (*Atti R. Accad. Lincei*, 1906, [v], **15**, i, 136—138).—The *lactone* of 1-*phenyl*-3-*hydroxyphenyl*-5-*methylpyrazole*-4-*carboxylic acid*,



$$NMe\!<\!\begin{array}{l}N{=\!=}C{\cdot}C_6H_4\\ \qquad\;\;|\\ CMe{:}C{-\!-}CO\end{array}\!\!>\!O,$$

obtained by condensing *o*-hydroxybenzaldehydephenylhydrazone with ethyl acetoacetate in presence of zinc chloride, crystallises from alcohol in slender, white needles melting at 182—183° and dissolves sparingly in ether or benzene and readily in chloroform or acetone.

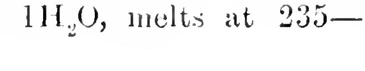
When heated with 10 per cent. potassium hydroxide solution, the lactone is converted into the corresponding *acid*,



$$NMe\!<\!\begin{array}{l}N{=\!=\!=}C{\cdot}C_6H_4{\cdot}OH\\ \qquad\quad\;|\\ CMe{:}C{\cdot}CO_2H\end{array},$$

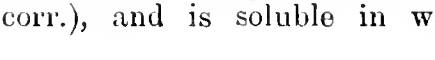
which crystallises from alcohol in slender, white needles melting and decomposing at about 160° and dissolves in benzene and very readily in chloroform, acetone, or ether. T. H. P.

5-Amino-4-ketodihydroquinazoline and 5-Amino-4-keto-2-methyldihydroquinazoline. MARSTON T. BOGERT and VICTOR J. CHAMBERS (*J. Amer. Chem. Soc.*, 1906, **28**, 207—213).—5-*Amino*-4-*ketodihydroquinazoline* (5-*amino*-4-*hydroxyquinazoline*),



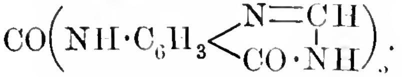
$$\begin{array}{l}CH{\cdot}CH{=\!=\!=}C{\cdot}N{=}CH\\ \|\qquad\qquad\quad\;|\qquad\;\;|\\ CH{\cdot}C(NH_2){:}C{\cdot}CO{\cdot}NH\end{array}$$

or

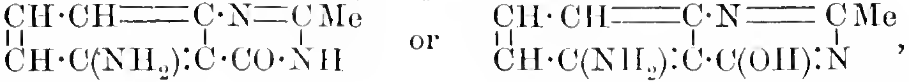


$$\begin{array}{l}CH{\cdot}CH{=\!=\!=}C{\cdot}N{=\!=\!=\!=}CH\\ \|\qquad\qquad\quad\;|\qquad\qquad\;|\\ CH{\cdot}C(NH_2){:}C{-\!-}C(OH){:}N\end{array},$$

prepared by the action of stannous chloride on 5-nitro-4-ketodihydroquinazoline (Abstr., 1905, i, 613), crystallises in long, slender needles with $1H_2O$, melts at 235—236° (corr.), and is soluble in water, alcohol, acetone, or ethyl acetate; it dissolves in solutions of alkali hydroxides and is reprecipitated by carbon dioxide. The *hydrochloride* crystallises in needles; the *platinichloride* crystallises with $2H_2O$. The *dibromo*-derivative, obtained as a flocculent precipitate by adding bromine water to a warm aqueous solution of the quinazoline, gradually darkens on exposure to light. *5-Acetylamino-4-ketodihydroquinazoline* forms colourless, slender needles, melts and darkens at 285—286° (corr.), is soluble in warm acetone or alcohol, and yields a bromo-derivative. The corresponding *benzoyl* derivative crystallises in white, lustrous needles and melts at 263—264° (corr.). *5-Phenylcarbamido-4-ketodihydroquinazoline*, obtained by the action of phenylcarbimide on the aminoquinazoline, forms slender, white needles and is easily soluble in warm alcohol and slightly so in warm benzene; when heated, it melts at 250—260° with formation of carbanilide and a substance which is probably the symmetrical *diquinazolylcarbamide*,


$$CO\left(NH\cdot C_6H_3<\begin{matrix}N{=}CH\\ CO\cdot NH\end{matrix}\right)_2.$$

5-Amino-4-keto-2-methyldihydroquinazoline,


$$\begin{matrix}CH\cdot CH{=\!=}C\cdot N{=}CMe\\ CH\cdot C(NH_2){:}C\cdot CO\cdot NH\end{matrix} \quad \text{or} \quad \begin{matrix}CH\cdot CH{=\!=}C\cdot N{=\!=}CMe\\ CH\cdot C(NH_2){:}C\cdot C(OH){:}N\end{matrix},$$

obtained by the reduction of 5-nitro-4-keto-2-methyldihydroquinazoline with stannous chloride, forms pale reddish-brown needles, melts and decomposes at 295—310°, slowly darkens on exposure to light, and is soluble in alcohol, acetone, or ethyl acetate; it dissolves in dilute alkali hydroxides and is reprecipitated by carbon dioxide or dilute acids. The *hydrochloride* and *platinichloride* were obtained as crystalline precipitates. E. G.

Thiazines. Robert Gnehm and Felix Kaufler (*Ber.*, 1906, **39**, 1016—1020. Compare Abstr., 1904, i, 687, 935; Gnehm and Schröter, this vol., i, 211; Kehrmann, Abstr., 1902, i, 566).—When heated with alcoholic ammonia in a sealed tube at 140—150° for four hours, methylene-blue hydrochloride yields *as-dimethyl-leucothionine*,


$$NMe_2\cdot C_6H_3<\begin{matrix}NH\\ S\end{matrix}>C_6H_3\cdot NH_2,$$

which crystallises from light petroleum in green needles, melts at about 160°, is readily soluble in benzene or toluene, and is rapidly oxidised by air to *as*-dimethylthionine; this is identical with Formánek's dye (Abstr., 1905, ii, 217). The *hydrochloride*, $C_{14}H_{14}N_3SCl$, is obtained as a dark blue, crystalline mass, and is readily soluble in water, forming a blue solution which becomes red on addition of an alkali hydroxide, or in boiling methyl or ethyl alcohol, forming an intensely blue solution with a bluish-red fluorescence.

When heated with benzylamine in alcoholic solution at 130—140° under pressure, methylene-blue forms *benzoylaminotetramethylthionine*, which is isolated in the form of its *iodide*, $C_{23}H_{25}N_4SI$; this forms a violet powder with metallic lustre; the *hydrochloride* is readily soluble in water or alcohol, forming a blue solution, the absorption spectrum of which resembles that of methylene-blue; on addition of an alkali hydroxide to the aqueous solution, a reddish-violet precipitate is formed.

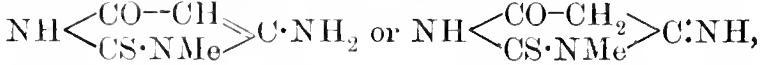
Successive treatment of dimethylthionine with sodium nitrite and potassium xanthate in hydrochloric acid solution leads to the formation of the *thioncarbonate* of thiazinemercaptan, which is obtained as a violet resin. When heated with 80 per cent. sulphuric acid on the water-bath, this evolves carbonyl sulphide and yields a bluish-black powder, which dissolves in sodium sulphite solution, forming the *leuco*-derivative; when warmed with this solution, washed, and exposed to the air, cotton-wool is dyed a dull blue. G. Y.

Methylene-green. ROBERT GNEHM and E. WALDER (*Ber.*, 1906, **39**, 1020—1022).—Methylene-green (nitromethylene-blue) is formed by the action of sodium nitrite, nitrogen trioxide, nitric oxide, or amyl nitrite on methylene-blue in dilute sulphuric or nitric acid solution. The *nitrate*, $C_{16}H_{17}O_2N_4S{\cdot}NO_3$, and *hydrobromide*,

$$C_{16}H_{17}O_2N_4SBr,2H_2O,$$

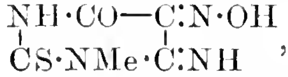
were analysed. G. Y.

3-Methylhypoxanthine. WILHELM TRAUBE and FRIEDRICH WINTER (*Arch. Pharm.*, 1906, **244**, 11—20).—Crystalline 4-*amino*-6-*oxy*-2-*thio*-3-*methylpyrimidine* (4-*amino*-2-*thio*-3-*methyluracil*),



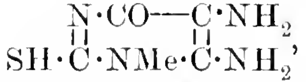
$$\mathrm{NH}{<}\begin{matrix}\mathrm{CO{-}{-}CH}\\ \mathrm{CS{\cdot}NMe}\end{matrix}{>}\mathrm{C{\cdot}NH_2}\ \text{or}\ \mathrm{NH}{<}\begin{matrix}\mathrm{CO{-}CH_2}\\ \mathrm{CS{\cdot}NMe}\end{matrix}{>}\mathrm{C{:}NH},$$

is obtained by boiling a solution of methylthiocarbamide in alcoholic sodium ethoxide with ethyl cyanoacetate. When a solution of it in normal aqueous sodium hydroxide is mixed with sodium nitrite and a large excess of acetic acid is added, 4-*imino*-5-iso*nitroso*-6-*oxy*-2-*thio*-3-*methylpyrimidine*,



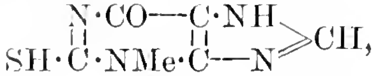
$$\begin{array}{l}\mathrm{NH{\cdot}CO{-}C{:}N{\cdot}OH}\\ \mathrm{\ |\qquad\quad\ |}\\ \mathrm{CS{\cdot}NMe{\cdot}C{:}NH}\end{array},$$

is precipitated. This crystallises in violet-green needles; its salts are red, and the ammonium salt is but sparingly soluble. When this substance is added gradually to boiling aqueous yellow ammonium sulphide and the liquid filtered finally, yellow 4 : 5-*diamino*-6-*oxy*-2-*thiol*-3-*methylpyrimidine*,



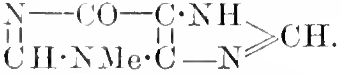
$$\begin{array}{l}\mathrm{\quad N{\cdot}CO{-}{-}C{\cdot}NH_2}\\ \mathrm{\quad\,\|\qquad\quad\ \|}\\ \mathrm{SH{\cdot}C{\cdot}NMe{\cdot}C{\cdot}NH_2}\end{array},$$

crystallises out as the liquid cools. When this is boiled with formic acid, a yellow *formyl* derivative gradually separates, and when the *potassium* salt of this, $C_6H_5ON_4SK,H_2O$ (obtained by dissolving the derivative in normal aqueous potassium hydroxide and precipitating with absolute alcohol), is heated at 250°, water is lost and crystalline 3-*methylthiohypoxanthine*,



$$\begin{array}{l}\mathrm{\quad N{\cdot}CO{-}{-}C{\cdot}NH}\\ \mathrm{\quad\,\|\qquad\quad\ \|}\\ \mathrm{SH{\cdot}C{\cdot}NMe{\cdot}C{-}{-}N}\end{array}{>}\mathrm{CH},$$

is formed. When this is warmed with 25 per cent. nitric acid, it is oxidised to crystalline 3-methylhypoxanthine,



$$\begin{array}{l}\mathrm{N{-}{-}CO{-}{-}C{\cdot}NH}\\ \mathrm{\|\qquad\qquad\ \|}\\ \mathrm{CH{\cdot}NMe{\cdot}C{-}N}\end{array}{>}\mathrm{CH}.$$

This substance dissolves in 210 parts of water, decomposes without melting when heated, forms well-crystallised salts with alkalis, dissolves readily in dilute mineral acids, and forms a crystalline platinichloride. The position of the methyl group is known from the fact that the 4-amino-6-oxy-2-thiomethylpyrimidine, when subjected to prolonged heating with aqueous hydrogen peroxide, yields a product identified as 4-amino-2 : 6-dihydroxy-3-methylpyrimidine (Abstr., 1901, i, 54). C. F. B.

Coupling of Benzidine with Aniline. Diphenylbisdiazoaminobenzene and Diphenylbisazoaminobenzene. Leo Vignon (*Compt. rend.*, 1906, **142**, 582—584).—When benzidine hydrochloride is diazotised and treated with aniline, dissolved in alcohol, in presence of sodium carbonate, or when diazobenzene chloride reacts with benzidine, (1) dissolved in cold alcohol in presence of sodium acetate, or (2) suspended in cold acetic acid, *diphenylbisdiazoaminobenzene*,

$$C_{12}H_8(N_2{\cdot}NHPh)_2,$$

is formed. This separates from benzene in yellowish-red crystals, melts at 180°, and is decomposed by 50 per cent. sulphuric acid, evolving much nitrogen. Its constitution was established by its hydrolysis into aniline and γ-dihydroxydiphenyl by boiling it with dilute sulphuric acid for fifteen minutes. When warmed with aniline and a small quantity of aniline hydrochloride, it is converted into *diphenylbisazoaminobenzene*, $C_{12}H_8(NH{\cdot}N_2Ph)_2$, which separates from alcohol as a reddish-yellow substance and melts at 158—159°. T. A. H.

Estimation of the Sugar Group in Proteids. Otto Krummacher (*Zeit. Biol.*, 1906, **47**, 612—627).—The views held regarding the origin of glycogen from proteid make it necessary to estimate the reducing substance in those proteids used as food in the experiments. Witte's peptone has been used in some of these experiments on rabbits. One hundred grams of dry Witte's peptone yielded 2·53 grams of reducing substance reckoned as glucosamine. Washed meat yielded 0·48 gram per cent. reckoned in the same way. The methods employed are described in full, and a large section of the paper is devoted to the study of the reducing power of glucosamine.

W. D. H.

Salts of Casein. John H. Long (*J. Amer. Chem. Soc.*, 1906, **28**, 372—384).—The equivalent weights of the casein of cow's milk and of goat's milk have been determined by titration with $N/10$ alkali hydroxide in presence of phenolphthalein and have been found to be 1124 and 1190 respectively. The greater equivalent weight of the casein of goat's milk indicates the presence of a small additional complex in the molecule or of some small group not readily separated in the preparation of the casein.

The electrical conductivity has been measured of solutions of the normal acid and basic sodium salts, the normal potassium and ammonium salts, and the normal and acid lithium salts of the casein of cow's milk, and of the normal sodium and potassium salts of the casein of goat's milk, and it has been found that the conductivities of the two forms of casein for equal amounts of alkali are nearly the same.

The sodium salt of the casein of goat's milk has $[\alpha]_D$ $-105°$ at $20°$, which is slightly larger than that given by the corresponding salt of the casein of cow's milk (compare Abstr., 1905, ii, 498). E. G.

Method for the Study of Proteolytic and Gelatinolytic Enzymes. CLAUDIO FERMI (*Arch. Hygiene*, 1906, **55**, 140—205).—The method described consists in estimating the exact numerical relationships of proteolytic ferment action by the method usually known as Mett's: the tubes are filled with gelatin, this being stated to be more sensitive than a number of other substances tried. In relation to trypsin action, the sensitiveness is increased by making the gelatin alkaline with sodium carbonate. The strength of the gelatin employed and certain other factors have also to be considered. The results are given in numerous tables. The paper contains a discussion on the question of priority in the use of the method, and also of the modification of gelatin plates sometimes employed. W. D. H.

Magnesium Compound of Organic Triphenylmethyl Chloride. Preparation of Triphenylmethane and Triphenylacetic Acid. JULIUS SCHMIDLIN (*Ber.*, 1906, **39**, 628—636. Compare Sachs and Ehrlich, Abstr., 1904, i, 196; Gomberg and Cone, Abstr., 1905, i, 641; Baeyer, *ibid.*, 766.)—Magnesium reacts with triphenylmethyl chloride in presence of iodine, in ethereal solution in an atmosphere of hydrogen, to form the crystalline *compound*, $CPh_3{\cdot}MgCl$, part of which remains dissolved as a yellow solution. The action of dry air on the magnesium compound in benzene solution leads to the formation of triphenylmethyl peroxide. When heated with dilute hydrochloric acid in an atmosphere of hydrogen in a reflux apparatus, the ethereal solution of the magnesium compound yields triphenylcarbinol, but the action of boiling hydrochloric acid on the solid magnesium compound, from which the ether has been distilled, leads to the formation of triphenylmethane, which is obtained in a yield of 78 per cent. of the triphenylmethyl chloride used. As triphenylmethyl chloride is prepared easily in good yields by Gomberg's method (Abstr., 1901, i, 77, 374), its conversion by means of its magnesium compound into triphenylmethane is the most advantageous method for the preparation of triphenylmethane.

Triphenylacetic acid is formed, together with small quantities of triphenylmethane, by the action of carbon dioxide on magnesium triphenylmethyl chloride in ethereal solution. The acid, which is obtained in a yield of 83 per cent. of the theoretical, crystallises from glacial acetic acid in long, glistening, white prisms and melts, decomposing to only a very slight extent, at 264—265°. G. Y.

Organic Chemistry.

Symmetrical Tertiary α Dinitroparaffins. Iwan I. Bewad and A. Pirinsky (*Ber.*, 1906, **39**, 1231—1238). The bromo derivatives of secondary nitroparaffins react readily with finely-divided (molecular) silver, either with or without the addition of dry ether, yielding *s*-di-*tert.*-nitroparaffins, with the two nitro-groups attached to adjacent carbon atoms, $2CBrRR'\cdot NO_2 + 2Ag = 2AgBr + NO_2\cdot CRR'\cdot CRR'\cdot NO_2$.

A 65—70 per cent. yield of *βγ* dinitro-*βγ*-dimethylbutane (*s-tert.* dinitrohexane), $NO_2\cdot CMe_2\cdot CMe_2\cdot NO_2$, may be obtained from *β* bromo-*β*-nitropropane. It crystallises from benzene in colourless, transparent plates or prisms, melts at 210·5—211·5°, is insoluble in water or light petroleum, and dissolves sparingly in ether. When gently warmed, it sublimes; it appears to be identical with the compounds described by Zelinsky (*J. Russ. phys. chem. Ges.*, 1894, **26**, 610) and by Konowaloff (Abstr., 1895, i, 633). When reduced with tin and hydrochloric acid, it yields the corresponding diamine. The *hydrochloride*,

$$C_6H_{12}(NH_2)_2,2HCl,$$

crystallises from dilute alcohol in colourless needles and decomposes at 310°. The *platinichloride*, $C_6H_{18}N_2PtCl_6,2H_2O$, crystallises in orange-yellow needles or plates and decomposes at 280°. The *aurichloride*, $C_6H_{16}N_2,2HAuCl_4,4H_2O$, forms large, transparent, yellow prisms or plates. The *base* melts at about 100° and distils at 147—149° under 740 mm. pressure. It is very volatile and also extremely hygroscopic, and dissolves with the greatest readiness in ether or water. Pinacolin is formed when an aqueous solution of the nitrite of the base is distilled.

γδ-Dinitro-γδ-dimethylhexane (s-tert.-*α-dinitro-octane*),

$$NO_2\cdot CMeEt\cdot CMeEt\cdot NO_2,$$

crystallises from ether in small, rectangular plates, melts at 79—80°, sublimes even at 40°, and dissolves readily in most organic solvents with the exception of light petroleum. The corresponding *diamine* yields a *hydrochloride* which begins to decompose at 270°, a *platinichloride*, $C_8H_{22}N_2PtCl_6,5H_2O$, and an *aurichloride*,

$$C_8H_{20}N_2,2HAuCl_4,2H_2O,$$

which, in the anhydrous form, melts and decomposes at 198—200°.

J. J. S.

Preparation of Aldehyde-free Alcohol for Use in Oil and Fat Analysis. Frederick L. Dunlop (*J. Amer. Chem. Soc.*, 1906, **28**, 395—398).—Mere treatment with potassium hydroxide and distillation does not lead to the desired result. The following process is therefore recommended.

To 1 litre of 95 per cent. alcohol are added 1·5 grams of silver nitrate dissolved in 3 c.c. of water. To this are then added very slowly 3 grams of potassium hydroxide dissolved in 15 c.c. of hot alcohol. Without shaking, the liquid is allowed to remain until the silver precipitate has completely settled, and the clear liquid is then submitted to distillation, when a perfectly neutral alcohol free from aldehyde is obtained.

L. de K.

Action of Organo-magnesium Compounds on Crotonaldehyde. Jean Reif (*Ber.*, 1906, 1603—1604).—Magnesium ethyl bromide and crotonaldehyde in ethereal solution yield a product from which Δ^{β}-*hexene-δ-ol*, CHMe:CH·CHEt·OH, is obtained on the addition of cold dilute sulphuric acid. The alcohol is a colourless, mobile liquid, and distils at 85—87° under 120 mm. pressure, or at 133—134° under atmospheric pressure. The *acetate* distils at 153—155°, the chloride, δ-*chloro*-Δ^{β}-*hexene*, $C_6H_{11}Cl$, at 122—126°, and δ *methoxy*-Δ^{β}-*hexene*, $C_7H_{14}O$, at 110—113°.

From magnesium propyl bromide, Δ^{β}-*heptene-δ-ol*, CHMe:CHPr·OH, is formed: it distils at 152—154°, or at 104—105° under 120 mm. pressure. The *acetate*, $C_9H_{16}O_2$, distils at 168—170°. J. J. S.

Derivatives of Pyrophosphoric Acid. Jacques Cavalier (*Compt. rend.*, 1906, **142**, 885—887. Compare Abstr., 1904, ii, 658).—Ethyl, *n*-propyl, *iso*propyl, *n*-butyl, amyl, and allyl pyrophosphates have been prepared by the action of silver pyrophosphate on the corresponding alkyl iodide. The esters are liquid at the ordinary temperature, decompose when heated, and cannot be distilled. They are soluble in benzene, carbon disulphide, carbon tetrachloride, and ether. Ethyl pyrophosphate is also soluble in water, but the solution has a strongly acid reaction, indicating either hydrolysis or formation of an orthophosphoric derivative. The cryoscopic determination of the molecular weights of the esters in benzene solution gave values corresponding with the formula $R_4P_2O_7$. In the case of the *iso*propyl and allyl esters, which were obviously impure, the molecular weight values were greater than those required by theory. H. M. D.

Composition of Petroleum. Sulphur Compounds and Unsaturated Hydrocarbons in Canadian Petroleum. Charles F. Mabery and William O. Quayle (*Amer. Chem. J.*, 1906, **35**, 404—432. Compare Mabery and Smith, Abstr., 1891, 1172).—A series of sulphur compounds has been isolated from Canadian petroleum by fractional distillation and subsequent treatment with alcoholic mercuric chloride. The mercuric chloride precipitates are obtained in the crystalline form from the lower fractions and as viscous or oily masses from the less volatile portions. The sulphur compounds are regenerated from the mercuric chloride precipitates by means of hydrogen sulphide and are further purified by fractional distillation. The substances are members of a new series for which the name "thiophan" is suggested. They combine with chloroplatinic acid with formation of heavy, viscous oils. When the thiophans are heated with ethyl iodide in a sealed tube, additive *compounds*, $C_nH_{2n}S,EtI$, are formed, which crystallise in small prisms and, when warmed with silver oxide and water, are converted into the corresponding hydroxides, which have an alkaline reaction. The thiophans combine violently with bromine with evolution of a quantity of hydrogen bromide equivalent to that of the bromine added, and are readily oxidised by potassium permanganate or chromic acid with formation of sulphones. In empirical composition, the thiophans correspond with hydrothiophens which have not hitherto been synthesised, but their constitution has not yet been established. The following compounds have been isolated.

Heptylthiophan, $C_7H_{14}S$, boils at 74—76° under 50 mm. or at 158—160° under 750 mm. pressure, has a sp. gr. 0·8878 at 20°, and n_D 1·468.

Octylthiophan, $C_8H_{16}S$, boils at 81—83° under 50 mm. or at 167—169° under atmospheric pressure, has a sp. gr. 0·8929 at 20°, and n_D 1·4860.

iso*Octylthiophan* boils at 94—96° under 50 mm. or at 183—185° under atmospheric pressure, and has a sp. gr. 0·8937 at 20°.

Nonylthiophan, $C_9H_{18}S$, boils at 106—108° under 50 mm. or at 193—195° under atmospheric pressure, has a sp. gr. 0·8997 at 20°, and n_D 1·4746.

Decylthiophan, $C_{10}H_{20}S$, boils at 114—116° under 50 mm. or at 207—209° under 750 mm. pressure, has a sp. gr. 0·9074 at 20°, and n_D 1·4766.

Undecylthiophan, $C_{11}H_{22}S$, boils at 128—130° under 50 mm. pressure, has a sp. gr. 0·9147 at 20°, and n_D 1·480.

Tetradecylthiophan, $C_{14}H_{28}S$, boils at 168—170° under 50 mm. or at 266—268° under 750 mm. pressure, has a sp. gr. 0·9208 at 20°, and n_D 1·4892.

Hexadecylthiophan, $C_{16}H_{32}S$, boils at 184—186° under 50 mm. or at 283—285° under 750 mm. pressure, has a sp. gr. 0·9222 and n_D 1·4903.

Octadecylthiophan, $C_{18}H_{36}S$, boils at 198—202° under 50 mm. and at 290—295° under atmospheric pressure, has a sp. gr. 0·9235 at 20°, and n_D 1·4977.

The following sulphones have been prepared. *Hexylthiophansulphone*, $C_6H_{12}SO_2$, is a thick, viscous oil, which has a sweet taste and odour. *Heptylthiophansulphone*, $C_7H_{14}SO_2$, is a thick, heavy oil, which has a sp. gr. 1·1138 at 20°. *Octylthiophansulphone*, $C_8H_{16}SO_2$, has a sp. gr. 1·1142 at 20°. *Nonylthiophansulphone*, $C_9H_{18}SO_2$, has a sp. gr. 1·1161 at 20°. *Undecylthiophansulphone*, $C_{11}H_{22}SO_2$, has a sweet, pleasant odour and a sp. gr. 1·1126 at 20°. *Dodecylthiophansulphone*, $C_{12}H_{24}SO_2$, obtained by the action of potassium permanganate on the distillate boiling at 142—144° under 50 mm. pressure, has a sp. gr. 1·1372 at 20°.

Canadian petroleum contains a small proportion of unsaturated hydrocarbons, probably of the ethylene series. These compounds were identified by converting them into the corresponding alkyl bromides by heating them with fuming hydrobromic acid. The fraction boiling at 70—80° under atmospheric pressure yielded a *hexyl bromide* which boiled at 62—65° under 50 mm. pressure. The fraction boiling at 98—102° under atmospheric pressure furnished a *heptyl bromide* which boiled at 76—80° under 50 mm. pressure and had a sp. gr. 1·1601. The fraction boiling at 118—119° under atmospheric pressure gave an *octyl bromide* which boiled at 93—95° under 50 mm. pressure and had a sp. gr. 1·1836. The fraction boiling at 140—141° under atmospheric pressure yielded a *nonyl bromide* which boiled at 110—113° under 50 mm. pressure and had a sp. gr. 1·2084.

Canadian petroleum also contains other hydrocarbons which differ in odour and in other respects from those hitherto identified in petroleum, and are possibly terpenes. E. G.

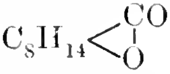
Dehydration of β-Hydroxy-β-Alkylpivalic Esters. ALFRED P. COURTOT (*Bull. Soc. chim.*, 1906, [iii], **35**, 217—223. Compare this vol., i, 230).—*Ethyl hydroxyethylpivalate* (ethyl β-hydroxy-αα-dimethylvalerate), prepared by condensing propaldehyde with ethyl bromo*iso*butyrate, is a viscous liquid of pleasant odour and boils at 106° under 20 mm. pressure. The *acetyl* derivative boils at 127—128° under 37 mm. pressure. The free *acid*, $OH{\cdot}CHEt{\cdot}CMe_2{\cdot}CO_2H$, crystallises from boiling ether, melts at 94°, and boils at 150—151° under 15 mm. pressure. The *calcium* and *copper* salts are crystalline. The *phenylcarbamate* crystallises from boiling water in long needles, melts at 100—101°, and is insoluble in benzene or light petroleum. When ethyl β-hydroxy-αα-dimethylvalerate, dissolved in benzene, is treated with phosphoric oxide, it yields *ethyl αα-dimethylpropenylacetate* [*αα-dimethyl-Δ^{β}-pentenoate*], $CHMe{:}CH{\cdot}CMe_2{\cdot}CO_2Et$, and αα-dimethylvalerolactone. The former is a colourless, mobile liquid of pleasant odour and boils at 162°. The free acid, identical with Perkin and Smith's crotonyldimethylacetic acid (Trans., 1904, **85**, 156), melts at −17° to a mobile liquid and boils at 119° under 24 mm. pressure. The *calcium*, *lead*, and *zinc* salts are crystalline. The *benzylamine* salt crystallises from ether and melts at 90°. The *amide* of the acid crystallises from a mixture of ether and light petroleum in silky spangles and melts at 88°, the *anilide* forms long needles from light petroleum and melts at 56°, the *phenylhydrazide* crystallises from ether and melts at 125—126°, and the *benzylamide*, obtained by heating molecular proportions of the acid and benzylamine at 180° for six hours, is a viscous liquid and boils at 190° under 20 mm. pressure. The *chloride* of the acid is a mobile liquid and boils at 56° under 21 mm. pressure. On reduction, dimethyl-Δ^{β}-pentenoic acid yields the corresponding *ββ-dimethyl-Δ^{γ}-pentenol*, $CHMe{:}CH{\cdot}CMe_2{\cdot}CH_2{\cdot}OH$, a liquid of pleasant odour boiling at 150°. The *acetyl* derivative boils at 167—168°. β-Bromo-αα-dimethylvalerolactone, obtained by brominating dimethylhexenoic acid in chloroform, crystallises from ether, melts at 90°, and boils at 120° under 20 mm. pressure (compare Perkin and Smith, *loc. cit.*). T. A. H.

Antimony Derivatives of Thioglycollic Acid. LUDWIG RAMBERG (*Ber.*, 1906, **39**, 1356—1358).—The compound

$$CO_2H{\cdot}CH_2S{\cdot}Sb{<}\begin{matrix}O{\cdot}CO\\ \vert\\ S{\cdot}CH_2\end{matrix}$$

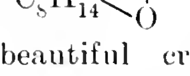
(compare Klason and Carlson, this vol., i, 232) is a moderately strong acid, but cannot be estimated volumetrically, as the end reaction is not sharp on account of partial hydrolysis of the internal ester. The *sodium*, *potassium*, and *barium* salts are described. The antimony cannot be estimated by electrolysis, but it is completely precipitated by hydrogen sulphide from a solution of the sodium salt. C. S.

Characteristic Reaction of Ethyl Glyoxylate. Action of Ammonia on the Ester and its Derivatives. LOUIS J. SIMON and G. CHAVANNE (*Compt. rend.*, 1906, **142**, 930—933).—When ethyl glyoxylate is heated with aqueous ammonia, a coloured substance with strong tinctorial properties is formed in accordance with the equation $2COH\cdot CO_2Et + 3NH_3 = 2C_2H_5OH + C_4H_9O_4N_3$. The substance is black in colour, slightly soluble in water, insoluble in alcohol; it dissolves in ammonia and in solutions of the alkali hydroxides and carbonates with a deep red coloration. The formation of a coloured substance appears to be quite characteristic of ethyl glyoxylate; it does not take place with the esters of acids closely related to glyoxylic nor with glyoxylic acid itself. The authors suggest that the coloured substance is the ammonium salt of the compound  $OH\cdot CH<\begin{matrix}CO\cdot NH\\NH\cdot CO\end{matrix}>CH\cdot OH$, formed by condensation of two molecules of glyoxylamide. H. M. D.

Camphoric Acid. XV. Certain Derivatives of Aminolauronic Acid. William A. Noyes and René de M. Taveau (*Amer. Chem. J.*, 1906, **35**, 379—386. Compare Abstr., 1904, i, 807).—When the nitroso-derivative of aminolauronic anhydride (1 mol.) is boiled with aqueous 10 per cent. sodium hydroxide (1·5 mols.), the following substances are produced: hydrocarbon, C_8H_{14}, 27·8 per cent.; *iso*campholactone, 21·4 per cent.; an unsaturated acid, $C_8H_{13}\cdot CO_2H$, 6·6 per cent.; liquid acids, probably consisting largely of γ-lauronolic acid, 1·4 per cent.; hydroxylauronic acid, 1·7 per cent.; a new lactone,  $C_8H_{14}<\begin{matrix}CO\\|\\O\end{matrix}$, 4·0 per cent.

*iso*Campholactone boils at 123·4° under 28 mm. and at 125·6° under 30 mm. pressure. The *methyl ester* of the corresponding hydroxy-acid, $OMe\cdot C_8H_{14}\cdot CO_2H$, obtained by the action of methyl iodide on the silver salt, boils at 150—153° under 19 mm. pressure, crystallises in needles, and melts at 84°.

The unsaturated acid, $C_8H_{13}\cdot CO_2H$, forms a white, curdy mass, boils, or rather sublimes, at 130—133° under 21 mm. pressure, melts at 152—154°, is readily oxidised by potassium permanganate, and is probably identical with the acid obtained by Walker and Henderson (Trans., 1895, **37**, 343) from the mixture of esters formed by the electrolysis of potassium *allo*-ethyl camphorate. The *silver* and *calcium* salts are described.

The new *lactone*,  $C_8H_{14}<\begin{matrix}CO\\|\\O\end{matrix}$, boils at about 126° under 27 mm. pressure, forms beautiful crystals, melts at 164—165°, has $[\alpha]_D$ + 13·87°, and is insoluble in strong potassium carbonate solution. The corresponding *hydroxy-acid*, $OH\cdot C_8H_{14}\cdot CO_2H$, melts and decomposes at 189·5°; its *barium* salt crystallises with $4H_2O$. E. G.

Capacity of Ethoxy-groups for Substitution by Radicles. Synthesis of Acetal-esters and of Homologous Ethyl Ethoxyacrylates. Alexei E. Tschitschibabin (*J. pr. Chem.*, 1906, [ii], **73**, 326—336. Compare Reformatsky, this vol., i, 136; Sokolowsky, *ibid.*, 138).—Sokolowsky's supposed triethyl *s*-trimethylbutanetricarboxylate, formed by the action of zinc and ethyl α-bromopropionate on ethyl orthoformate, is *ethyl* as-*ββ-diethoxy*iso*butyrate*, $CH(OEt)_2\cdot CHMe\cdot CO_2Et$; when hydrolysed with 10 per cent. potassium hydroxide and neutralised carefully with hydrochloric acid, it yields a viscid liquid consisting of *as-ββ-diethoxyisobutyric acid*,

$$CH(OEt)_2\cdot CHMe\cdot CO_2H,$$

together with a small quantity of Sokolowsky's acid melting at 109°, which is β-ethoxy-α-methylacrylic acid. When distilled, the acetal acid decomposes, leaving a small residue of β-ethoxy-α-methylacrylic acid, and yielding carbon dioxide and *ethyl propenyl ether*, $CHMe\colon CH\cdot OEt$, which boils at 68—72°, and forms an *additive* compound with bromine, and αα-diethoxypropane, boiling at 122°. Ethyl propenyl ether and αα-diethoxypropane are hydrolysed readily by acids, forming propaldehyde and alcohol. The acetal-acid, which yields propaldehyde when distilled when dilute sulphuric acid, forms soluble uncrystallisable salts, of which those of the heavy metals are unstable in aqueous solution.

β-Ethoxy-α-methylacrylic acid, $OEt\cdot CH\colon CMe\cdot CO_2H$, is formed, together with small amounts of ethyl formylpropionate, by the action of cold dilute hydrochloric acid on ethyl *as*-ββ-diethoxy*iso*butyrate; it crystallises from light petroleum in large prisms, is hydrolysed by mineral acids, forming propaldehyde, alcohol, and carbon dioxide, and when boiled decomposes slowly into ethyl propenyl ether and carbon dioxide. The *ethyl* ester, formed by boiling the silver salt with ethyl iodide, boils at 200—201°, has the sp. gr. 0·9753 at 20°/0°, and has an odour differing from that of the acetal-ester.

The action of zinc and ethyl bromoacetate on ethyl orthoformate leads to the formation of β-ethoxyacrylic acid, $OEt\cdot CH\colon CH\cdot CO_2H$, which crystallises in colourless prisms, melts at 110·5°, and is identical with Otto's ethoxyacrylic acid (Abstr., 1890, 957; compare Claisen, Abstr., 1898, i, 421). It is hydrolysed readily by mineral acids, forming acetaldehyde, alcohol, and carbon dioxide; the *silver* salt, $C_5H_7O_3Ag$, is obtained as a white powder; the *ethyl* ester, $OEt\cdot CH\colon CH\cdot CO_2Et$, boils at 195—196° and has the sp. gr. 0·9983 at 20° 0° or 1·0174 at 0°/0°. G. Y.

Anhydrides of Diethylmalonic Acid. ALFRED EINHORN and HEINRICH VON DIESBACH (*Ber.*, 1906, **39**, 1222—1223).—A duodecimolecular *diethylmalonic anhydride*, $\left(CEt_2{<}{CO \atop CO}{>}O\right)_{12}$, is formed when diethylmalonyl chloride is treated with a dilute aqueous solution of pyridine; it is obtained as a slightly yellow, amorphous powder, melts at 80—85°, and decomposes when heated above its melting point. It dissolves in dilute potassium hydroxide, and is converted by ammonia into diethylmalonic acid, diethylmalonamide, and *diethylmalonamic acid*, $NH_2\cdot CO\cdot CEt_2\cdot CO_2H$, which crystallises in glistening, white, tetragonal plates, melts at 146°, forming carbon dioxide and diethylacetamide. The action of diethylamine on the anhydride at the ordinary temperature leads to the formation of diethylmalonic acid, *diethylmalondiethylamic acid*, $NEt_2\cdot CO\cdot CEt_2\cdot CO_2H$, which crystallises in long prisms and melts at 88—90°, and *diethylacetyldiethylamide*, which is obtained as a colourless oil. This, which is the main product when the reacting mixture is not cooled, has an odour of menthol and boils at 108° under 12 mm. pressure.

If the amorphous anhydride is boiled in an indifferent solvent it is decomposed, forming carbon dioxide, α-ethylbutyric anhydride boiling at 226—229°, and the *quadrimolecular anhydride* of diethylmalonic acid, $\left(\mathrm{CEt_2}\!<\!\begin{smallmatrix}\mathrm{CO}\\ \mathrm{CO}\end{smallmatrix}\!>\!\mathrm{O}\right)_4$, which crystallises from ethyl acetate in rhombic plates, melts and decomposes at 220°, and behaves towards alkali hydroxides, ammonia, and diethylamine in the same way as the amorphous anhydride. G. Y.

Synthesis of ββ-Dimethyl- and ββε-Trimethyl-pimelic Acids. GUSTAVE BLANC (*Compt. rend.*, 1906, 142, 996—999).—ββ-Dimethylvalerolactone, obtained by reducing ββ-dimethylglutaric anhydride (Abstr., 1905, i, 681), reacts with phosphorus pentabromide and alcohol to form *ethyl δ-bromo-ββ-dimethylvalerate*,

$$\mathrm{CH_2Br{\cdot}CH_2{\cdot}CMe_2{\cdot}CH_2{\cdot}CO_2Et},$$

which is a colourless oil boiling at 119° under 10 mm. pressure; the corresponding *acid* crystallises from ether in large prisms melting at 58°. Ethyl δ-bromo-ββ-dimethylvalerate condenses readily with ethyl sodiomalonate when heated under pressure at 100° to form the corresponding *tricarboxylic ester*, $\mathrm{CH(CO_2Et)_2{\cdot}(CH_2)_2{\cdot}CMe_2{\cdot}CH_2{\cdot}CO_2Et}$, which boils at 180° under 7 mm. pressure and yields ββ-dimethylpimelic acid on heating with hydrochloric acid (compare Léser, Abstr., 1899, i, 743).

Ethyl δ-bromo-ββ-dimethylvalerate condenses with ethyl sodiomethylmalonate to form the corresponding *tricarboxylic ester*, which boils at 180—182° under 7 mm. pressure; the corresponding *acid*, $\mathrm{CMe(CO_2H)_2{\cdot}[CH_2]_2{\cdot}CMe_2{\cdot}CH_2{\cdot}CO_2H}$, melts at 163°, and on heating at 180° is converted quantitatively into ββε-trimethylpimelic acid melting at 55—56°. M. A. W.

αγ-Dimethyl- and α-Ethyl-itaconic Acids. FRITZ FICHTER and CARL SCHLAEPFER (*Ber.*, 1906, 39, 1535—1536).—Both acids formed by boiling methylethylmaleic anhydride with sodium hydroxide (Fichter and Rudin, Abstr., 1904, i, 473) yield anhydrides when treated with acetyl chloride, and must belong to the itaconic acid series. The acid melting at 202°, and termed previously methylethylfumaric acid, is αγ-dimethylitaconic acid,

$$\mathrm{CHMe{:}C(CO_2H){\cdot}CHMe{\cdot}CO_2H},$$

as it is formed also by the action of sodium ethoxide on αγ-dimethylparaconic acid. The acid melting at 150°, and previously termed αγ-dimethylitaconic acid, is α-ethylitaconic acid,

$$\mathrm{CH_2{:}C(CO_2H){\cdot}CHEt{\cdot}CO_2H}.$$

αγ-Dimethylitaconic anhydride, 
$\begin{array}{l}\quad\;\;\mathrm{CHMe{\cdot}CO}\\ \mathrm{CHMe{:}\overset{|}{C}\text{———}CO}\end{array}\!\!>\!\mathrm{O}$, is a colourless oil which boils at 131° under 16 mm. pressure, and when boiled with water yields the acid melting at 202°.

α-Ethylitaconic anhydride, 
$\begin{array}{l}\quad\;\;\mathrm{CHEt{\cdot}CO}\\ \mathrm{CH_2{:}\overset{|}{C}\text{———}CO}\end{array}\!\!>\!\mathrm{O}$, crystallises from light petroleum, melts at 52°, and when boiled with water is hydrolysed to the acid melting at 150°. G. Y,

Conversion of Cholic Acid into Cholamine. THEODOR CURTIUS (*Ber.*, 1906, **39**, 1389—1391).—The *carbamate*, $C_{23}H_{39}O_3 \cdot NH \cdot CO_2Et$, is obtained when cholazide, $C_{23}H_{39}O_3 \cdot CON_3$, is boiled with absolute alcohol; it crystallises from ethyl acetate in small, doubly-refracting prisms, sinters at 125°, and melts and decomposes at 150°. By distillation in a vacuum with lime, it yields *cholamine*, $C_{23}H_{39}O_3 \cdot NH_2$, which separates from ethyl acetate in small, doubly-refracting, yellow needles; the aqueous solution is distinctly alkaline and has a bitter taste. The *hydrochloride*, $C_{23}H_{41}O_3N,HCl$, is an amorphous, yellow powder which becomes brown at 80°, melts at 120°, and decomposes at 140°. The *platinichloride*, $(C_{23}H_{41}O_3N)_2,H_2PtCl_6$, is a yellow powder which becomes brown at 180° and melts at 193° to a dark brown liquid.

From the amine, an aldehyde, $C_{22}H_{37}O_2 \cdot CHO$, cannot be obtained by the elimination of ammonia, proving that the carboxyl group in cholic acid is not attached to CH(OH). C. S.

New Method for the Preparation of Ketones. HUGO HAEHN (*Ber.*, 1906, **39**, 1702—1705).—When dry fatty acids are passed through a tube packed with calcium carbide and warmed in a furnace, ketones are produced: $2R \cdot CO_2H = COR_2 + CO_2 + H_2O$. Formic acid yields carbon monoxide and water; acetic acid, a mixture of acetone and methyl alcohol; propionic acid gives diethyl ketone, and butyric acid, dipropyl ketone in 30 per cent. yield. *iso*Valeric acid gives valerone and small quantities of valeraldehyde. Benzoic acid and calcium carbide react at a low red heat, best under 20 mm. pressure, with the formation of benzophenone. C. S.

Stable Compounds of Hyposulphites with Ketones. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 162875).—Solutions of hyposulphites are rendered more stable by addition of acetone, and this method has been employed to preserve them. It is now found that solid compounds of hyposulphites with acetone or methyl ethyl ketone are formed in the presence of alkalis, preferably sodium hydroxide and ammonia. The products obtained on evaporating the solution resist a temperature of 50° without deterioration. Those obtained in the absence of ammonia are less stable. Solutions of the ketone compounds only reduce indigotin slowly in the cold, more rapidly on warming. C. H. D.

Syntheses with *d*-Gluconic Acid. CARL PAAL and FRANZ HÖRNSTEIN (*Ber.*, 1906, **39**, 1361—1364).—With the object of adding hydrocarbon residues to the carbon chain of pentoses and hexoses by the action of Grignard's reagents on the corresponding lactones (compare Houben, Abstr., 1904, i, 334), the authors have prepared, by heating *d*-gluconic acid (1 mol.) and acetic anhydride (4 mols.) on the water-bath, a gum which they regard as a mixture of tetra-acetyl-*d*-gluconolactone and triacetyl-*d*-gluconolactone-ethylglucoside, having in alcoholic solution, after twenty-four hours, $[\alpha]_D$ 50·9°. The action on this mixture of an excess (12 mols.) of magnesium phenyl bromide, in ether-benzene solution, leads to the formation of diphenylmethylcarbinol and *αβγδεζ-hexahydroxy-αα diphenylhexane* (*αα-diphenyl d sorbitol ?*), $OH{\cdot}CH_2{\cdot}[CH{\cdot}OH]_4{\cdot}CPh_2{\cdot}OH$. The two compounds are separated, after removal of the ether and benzene, by solution of the former in light petroleum; the residual grey mass, after repeated crystallisation from ethyl acetate or absolute alcohol, is obtained in white needles. The substance melts at 154—157° and in alcoholic solution has $[\alpha]_D$ 77·9°. C. S.

Condensation of Formaldehyde. OSCAR LOEW (*Ber.*, 1906, **39**, 1592—1593. Compare Abstr., 1888, 358; 1889, 581; Euler and Euler, this vol., i, 142).—A claim for priority. G. Y.

Part played by Formaldehyde in the Caramelisation of Sugar. AUGUSTE TRILLAT (*Chem. Centr.*, 1906, i, 978; from *Bull. Assoc. Chim. Sucr. Dist.*, **23**, 652—655. Compare this vol., i, 234, 235).—A portion of the formaldehyde which is formed when sugar is heated polymerises and forms products which are analogous to methylenitan or formose, and the caramel itself may possibly be formed from these polymerides. This hypothesis is supported by the fact that when solutions of formaldehyde are treated with small quantities of alkali or metallic oxide at higher temperatures, a brown, amorphous substance is formed which has the same taste and odour, and apparently all the properties of the caramel which is obtained from sugar. When 100 parts of formaldehyde are heated with 4—5 parts of alkali, the action is complete in a few minutes. E. W. W.

Acidic Properties of Starch. EM. DEMOUSSY (*Compt. rend.*, 1906, **142**, 933—935).—The acidic properties of rice starch have been examined by allowing it to remain in contact with solutions of sodium, calcium, and barium hydroxides, of ammonia and sodium carbonate, and measuring the diminution of the alkali titre of the solutions. The diminution is considerable in the case of the hydroxide solutions, but much smaller with ammonia; the absorbed alkali can again be extracted with water. In the case of sodium carbonate, the diminution of the alkali titre is accompanied by the formation of an equivalent quantity of sodium hydrogen carbonate. Sodium chloride, potassium chloride, phosphate, and sulphate are all absorbed by starch. Copper acetate is absorbed to a much greater extent than the sulphate, and this is attributed to the weaker acid contained in it. Zinc and copper are taken up from ammoniacal solutions of the sulphates. The product obtained with copper is relatively stable; water extracts ammonia but no appreciable amount of copper from it. An ammoniacal solution of lead acetate shows no trace of dissolved lead after a few hours' contact with starch. Colloidal ferric oxide is also readily absorbed. The phenomena are attributed to the acidic character of the hydroxyl groups in the starch molecule. H. M. D.

[Hydrolysis of] some Celluloses. ADOLF ERNEST (*Zeit. Zuckerind. Böhm.*, 1906, **30**, 279—282).—Sugar beet cellulose was dissolved in strong sulphuric acid (250 grams) and water (84 grams to 100 grams of substance), diluted with water until the strength of the acid was

4 per cent., and heated at 95—97°. Ramie cellulose was hydrolysed in a similar manner. Both substances yielded only dextrose.

N. H. J. M.

Compounds of Palladous Haloids with Aliphatic Amines. ALEXANDER GUTBIER and A. KRELL (*Ber.*, 1906, **39**, 1292—1299. Compare Abstr., 1905, i, 876; ii, 584).—When a 33 per cent. solution of a primary alphylamine is added slowly to an excess of palladous chloride or bromide solution, a precipitate corresponding in composition with Vauquelin's salt, $Pd(NH_3)_4X_2,PdX_2$, is thrown down in the form of rose-red needles. Chlorides and bromides have been prepared by using methylamine, ethylamine, propylamine, and *iso*butylamine.

These salts are readily transformed into palladosammine derivatives; (1) when heated at about 200°; (2) when their aqueous solutions are evaporated; (3) by solution in warm alkali and precipitation with a solution of the requisite halogen hydride.

When solutions of the palladosammine chlorides or bromides are shaken with moist silver oxide, yellow solutions are obtained; these have a strongly alkaline reaction, can decompose ammonium salts, and contain the palladosammine hydroxides. All the palladosammine compounds are coloured: the chlorides pale yellow, the bromides dark yellow, and the iodides brownish-yellow. They all dissolve in concentrated ammonium hydroxide, yielding colourless solutions which contain palladosammine chloride, bromide, or iodide. The compounds are all of the type PdR_2X_2, where R = a molecule of the amine and X = Cl, Br, or I. Those described contain methylamine, ethylamine, propylamine, *iso*butylamine, dimethylamine, and diethylamine. The iodides of the two last mentioned are extremely unstable and could not be isolated.

Double chlorides and bromides of the type $PdCl_2,2MeNH_2,2HCl$ have been prepared from methylamine, ethylamine, propylamine, and *iso*butylamine. They form red or reddish-brown crystals and are not decomposed by water.

J. J. S.

Decomposition of Urotropine (Hexamethylenetetramine) R. ISCHIDZU and T. INOUYE (*Chem. Centr.*, 1906, i, 1087—1088; from *J. Pharm. Soc. Japan*, 1906, 1).—When urotropine, $C_6H_{12}N_4$, is decomposed by acids, the main products which contain carbon are formaldehyde and carbon dioxide. By the moderate action of hydrochloric or acetic acid for a certain time, urotropine (1 mol.) yields ammonia (2 mols.) and methylamine (2 mols.). When the concentration of the acid is increased, the temperature raised, or the duration of the action prolonged, the quantity of ammonia increases, whilst that of methylamine decreases. By distilling 100 parts of urotropine with dilute hydrochloric or sulphuric acid, ninety-five parts of formaldehyde are formed (theoretically 128); formaldehyde is also liberated by boiling with water. When urotropine is treated with saké, it is attacked by the free succinic, lactic, and acetic acids contained in the latter. When saké to which urotropine has been added is kept for some time, an appreciable quantity of formaldehyde is formed. Urotropine is more stable in alkaline than in neutral liquids.

E. W. W.

Glycine Picrate. PHOEBUS A. LEVENE (*J. Biol. Chem.*, 1906, 1, 413—414).—In the products of proteolysis, fractions containing glycine and alanine are easily obtained; from these, glycine is readily separable as a picrate; the method is stated to be simpler than Fischer's.

W. D. H.

Action of Nitrous Acid on Polyglycine Esters. I. Ethyl Diazoacetylaminoacetate. THEODOR CURTIUS and AUGUST DARAPSKY (*Ber.*, 1906, 39, 1373—1378).—*Ethyl diazoacetylaminoacetate*,

$$\mathrm{N_2{:}CH{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2Et},$$

is obtained when a small quantity of acetic acid or dilute sulphuric acid is added to mixed concentrated solutions of sodium nitrite and ethyl glycylglycine hydrochloride at 0°. It separates from alcohol in yellow leaflets, melts at 107°, and resembles ethyl diazoacetate in its reactions. It is reduced to hydrazine by ferrous sulphate and sodium hydroxide, reacts with iodine in ethereal solution to form *ethyl di-iodoacetylaminoacetate*, $\mathrm{CHI_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2Et}$, melting at 127—128°, and is converted by boiling water into *ethyl hydroxyacetylaminoacetate*, $\mathrm{OH{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2Et}$, which separates from benzene in colourless prisms and melts at 68·5°.

Ethyl acetylglycolylaminoacetate, $\mathrm{OAc{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2Et}$, obtained from ethyl diazoacetylaminoacetate and glacial acetic acid at 0°, forms colourless leaflets and melts at 88—89°. *Ethyl benzoylglycolylaminoacetate*, $\mathrm{OBz{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2Et}$, obtained by heating the diazo-compound with benzoic acid on the water-bath, forms small needles and melts at 94·5°. *Ethyl hippurylglycolylaminoacetate*,

$$\mathrm{NHBz{\cdot}CH_2{\cdot}CO_2{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2Et},$$

forms slender, glistening needles and melts at 88°.

Ethyl chloroacetylaminoacetate, obtained by passing hydrogen chloride into a dry ethereal solution of the diazo-compound, is identical with a substance described previously (Diels and Heintzel, Abstr., 1905, i, 174).

C. S.

Action of Nitrous Acid on Polyglycine Esters. II Ethyl Diazoacetylglycylaminoacetate. THEODOR CURTIUS and JAMES THOMPSON (*Ber.*, 1906, 39, 1379—1383).—*Ethyl diazoacetylglycylglycine*, $\mathrm{N_2{:}CH{\cdot}[CO{\cdot}NH{\cdot}CH_2]_2{\cdot}CO_2Et}$, is obtained when sodium nitrite and a small quantity of acetic acid acts on a solution of ethyl diglycylglycine hydrochloride and sodium acetate at 0°. It crystallises from alcohol in glistening, yellow leaflets, melts at 159—160°, and is decomposed by dilute mineral acids with evolution of nitrogen. *Ethyl di-iodoacetylglycylglycine*, $\mathrm{CHI_2{\cdot}[CO{\cdot}NH{\cdot}CH_2]_2{\cdot}CO_2Et}$, prepared from an alcoholic solution of the preceding compound and iodine, separates from alcohol in yellow needles and melts at 169°. Ethyl chloroacetylglycylglycine, obtained from the diazo-compound and hydrogen chloride in alcoholic solution, is identical with the compound obtained by Fischer and Otto (Abstr., 1903, i, 607). *Ethyl hydroxyacetylglycylglycine*, $\mathrm{OH{\cdot}CH_2{\cdot}[CO{\cdot}NH{\cdot}CH_2]_2{\cdot}CO_2Et}$, forms microscopic needles and melts at 108°. *Ethyl acetylglycolylglycylglycine*,

$$\mathrm{OAc{\cdot}CH_2{\cdot}[CO{\cdot}NH{\cdot}CH_2]_2{\cdot}CO_2Et},$$

prepared from the diazo-compound and acetic acid, forms microscopic, yellow crystals and melts at 124°. *Ethyl benzoylglycolylglycylglycine*, $\mathrm{OBz{\cdot}CH_2{\cdot}[CO{\cdot}NH{\cdot}CH_2]_2{\cdot}CO_2Et}$, melts at 131°. *Ethyl hippurylglycolylglycylglycine*, $\mathrm{NHBz{\cdot}CH_2{\cdot}CO_2{\cdot}CH_2{\cdot}[CO{\cdot}NH{\cdot}CH_2]_2{\cdot}CO_2Et}$, separates from hot water in colourless needles and melts at 148—149°.

Ethyl hippurylglycylglycolylglycylglycine,
$\mathrm{NHBz{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2{\cdot}CH_2{\cdot}[CO{\cdot}NH{\cdot}CH_2]_2{\cdot}CO_2Et}$,
obtained from the diazo- compound and an alcoholic solution of hippurylglycine, crystallises from hot water in white needles and melts and becomes brown at 204—205°. C. S.

Action of Nitrous Acid on Polyglycine Esters. III. Action of Ammonia on Ethyl Diazoacetylglycine and Ethyl Diazoacetylglycylglycine. THEODOR CURTIUS and JAMES THOMPSON (*Ber.*, 1906, **39**, 1383—1388. Compare Curtius and Gumlich, Abstr., 1904, i, 477).—*Diazoacetylglycinamide*, $\mathrm{N_2{:}CH{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO{\cdot}NH_2}$, is precipitated when ammonia is passed into ice-cold water containing ethyl diazoacetylglycine in suspension. It crystallises in yellow leaflets, melts and becomes brown at 160°, and is decomposed by dilute mineral acids or solutions of iodine with evolution of nitrogen. *Diazoacetylglycylglycinamide*, $\mathrm{N_2{:}CH{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO{\cdot}NH_2}$, similarly obtained, is a light yellow powder which melts and decomposes at 175°.

When excess of ammonium hydroxide is added to the foregoing amides or to the original esters without special cooling, colourless compounds are obtained with $\mathrm{NH_3}$ which do not evolve nitrogen by treatment with mineral acids or solutions of iodine. They are provisionally regarded as azomethane derivatives, for example,

$$\mathrm{NH}{<}\begin{smallmatrix}\mathrm{NH}\\ \mathrm{NH}\end{smallmatrix}{>}\mathrm{CH{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO{\cdot}NH_2}.$$

In cold concentrated aqueous solution they react with sodium nitrite and acetic acid to form an intensely violet solution from which ether extracts a substance which forms reddish-violet crystals, shows Liebermann's nitroso-reaction, and decomposes at 120°. C. S.

A New Type of Balanced Reactions. LOUIS J. SIMON (*Compt. rend.*, 1906, **142**, 790—791. Compare Abstr., 1902, i, 14).—The condensation of pyruvic acid and urethane to form diurethanepyruvic acid is a balanced reaction owing to the hydrolytic action of the water which forms the other product of the reaction. The dissociation of diurethanepyruvic acid by water increases (*a*) with the temperature; 100 c.c. of cold water require ten hours to hydrolyse 1·75 grams of the compound, whilst the reaction is completed in a few minutes at a gentle heat; (*b*) with the concentration, being complete in the most concentrated solutions, whilst solutions of lower concentrations contain equal numbers of dissolved and of dissociated molecules.

M. A. W.

Influence of the Juxtaposition of Ketonic and Acid Groups in the same Molecule. LOUIS J. SIMON (*Compt. rend.*, 1906, **142**, 892—894).—Dimethanepyruvic acid, which is decomposed by water, dissolves in ethyl alcohol without decomposition. By means of the alcoholic solution, the aniline, *p*-toluidine, and phenylhydrazine salts were prepared. The first two decompose at about 122° and 128°, the third melts without decomposing at 125°. When an aqueous solution of the phenylhydrazine salt is heated, the salt decomposes, the phenylhydrazone of pyruvic acid and urethane being formed.

Ethyl diurethanepyruvate, obtained by the action of hydrochloric acid on a mixture of pyruvic acid, urethane, and ethyl alcohol, is a crystalline substance which melts at 109°, distils without decomposition under reduced pressure, and dissolves readily in water. When heated with dilute acid, the ester is hydrolysed, and pyruvic acid, urethane, and alcohol are formed.

Potassium diurethanepyruvate, obtained by neutralising the acid, cannot be prepared by the action of urethane on potassium pyruvate. It is very soluble in water and ethyl alcohol, and contains $1\frac{1}{2}$ molecules of water of crystallisation which can be removed at 110—115°.

The observations show the influence of the juxtaposition of the ketonic and acid groups. H. M. D.

Ketone-cyanohydrins. HANS BUCHERER and ANDRÉ GROLÉE (*Ber.*, 1906, **39**, 1224—1227. Compare Abstr., 1903, i, 612).—*a*-Hydroxy*iso*butyronitrile and ethyl *β*-cyano-*β*-hydroxybutyrate are formed by the action of potassium cyanide on the sodium hydrogen sulphite compounds of acetone and ethyl acetoacetate in concentrated aqueous solution in yields of 96 per cent. and 97 per cent. of the theoretical respectively.

When pure, ethyl *β*-cyano-*β*-hydroxybutyrate is a reddish-yellow, heavy oil, which has no odour of hydrogen cyanide and is more stable than previously supposed (Morris, Trans., 1880, **37**, 6; Schiller-Wechsler, Abstr., 1885, 900). G. Y.

Dialkylmalonamides. KARL BÖTTCHER (*Ber.*, 1906, **39**, 1596. Compare Meyer, this vol., i, 137).—Better yields of the amides are obtained from the chlorides when the temperature is kept below 20°. The formation of *a*-methylbutyramide observed by Meyer was probably due to the presence of *a*-methylbutyryl chloride in the chloride used. J. J. S.

Solubility of Uric Acid in Silicic Acid, in Sodium Metasilicate, and in Distilled Water. EZIO COMANDUCCI (*Chem. Centr.*, 1906, i, 1091; from *Boll. Chim. Farm.*, **45**, 108—111).—Distilled water dissolves a larger quantity of uric acid in a day than water which contains 0·076 per thousand of silica or 0·12 of sodium silicate, Na_2SiO_3. The results of Gauthier's determinations of the solubility of uric acid in Mangiatorella water (*Calabria, Avanti!* 1904, 15 Sept.) may possibly be explained by the slow decomposition of the uric acid during the experiment and the subsequent solution of the decomposition products. E. W. W.

Action of Certain Gases on Potassium Thiocyanate at High Temperatures. JAROSLAV MILBAUER (*Zeit. anorg. Chem.*, 1906, **49**, 46—57. Compare Abstr., 1905, i, 121).—Potassium thiocyanate only undergoes slight dissociation into potassium cyanide and sulphur when kept for some hours at a bright red heat under diminished pressure. A similar result is obtained by heating in nitrogen and in carbon monoxide; these gases have no chemical action on the salt. In an atmosphere of hydrogen at a low red heat, decomposition occurs in approximate accordance with the equation: $4KCNS + 4H_2 = 2KCN + K_2S + 3H_2S + 2HCN$. The salt is also decomposed by water vapour at a high temperature with formation of potassium sulphide and carbonate and evolution of carbon dioxide, hydrogen sulphide, and ammonia. When heated in hydrogen sulphide, potassium cyanide, hydrogen cyanide, and sulphur are produced; in carbon dioxide at a low red heat, a little potassium cyanate is formed. The action of sulphur dioxide on the thiocyanate takes place in the following two stages: $2KCNS + 2SO_2 = K_2S + 2CO_2 + N_2 + 3S$ and $K_2S + 2SO_2 \rightleftharpoons K_2SO_4 + 2S$; the second reaction is reversible. G. S.

Complex Mercury Cobalt and Mercury Nickel Thiocyanates.

E. I. Orloff (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 1269—1272).—The salts described by the author were prepared by dissolving mercuric chloride and ammonium (or potassium) thiocyanate in water and adding to the compound, $(NH_4)_2Hg(CNS)_4$, thus formed, a solution of cobalt nitrate (or sulphate) or nickel nitrate.

The *cobalt* salt, $CoHg(CNS)_4$, forms beautiful blue crystals slightly soluble in water. Dilute hydrochloric or sulphuric acid has only little action on it, but aqueous alkali hydroxides decompose it, giving cobalt hydroxide and mercuric oxide. It may be used as a mineral pigment.

The *nickel* salt, $NiHg(CNS)_4,Hg(CNS)_2$, which is readily soluble in aqueous ammonium or potassium thiocyanate, forms a bluish-green powder.

Mixed nickel and cobalt salts of a dark green colour can also be obtained. T. H. P.

Absorption Spectra of Solutions of Isomeric Complex Cobalt Salts.

Arthur Rosenheim and Victor J. Meyer (*Zeit. anorg. Chem.*, 1906, **49**, 28—33).—As ammonium thiocyanate and thiocarbamide are isomeric, the *dithiocarbamide cobalt thiocyanate*, $Co(CSN_2H_4)_2(SCN)_2$, described by the authors (see this vol., i, 408) is isomeric with the *ammonium cobalt thiocyanate*, $(NH_4)_2Co(SCN)_4$, referred to in previous papers. For this reason it has been considered of interest to compare the absorption spectra of these two compounds dissolved in absolute alcohol.

The spectra of solutions of ammonium cobalt thiocyanate from 1/16 to 1/512 normal are qualitatively identical; there is no displacement of the region of absorption. It is considered that the absorptive power pertains to the bivalent ion $Co(SCN)_4^{\cdot\cdot}$, which remains stable on dilution. The isomeric dithiocarbamide cobalt thiocyanate shows an entirely different spectrum; the positions of maximum absorption vary greatly with the dilution, and in 1/128 normal solutions the absorptive power has practically disappeared. With the object of throwing light on the nature of the absorbing groups, measurements were also made with cobalt chloride hexahydrate and cobalt thiocyanate in alcoholic solution, and it was found that the spectrum of the latter salt closely resembles that of ammonium cobalt thiocyanate, whilst the entirely different spectrum of cobalt chloride corresponds in certain dilutions with that of the thiocarbamide compound. The authors discuss the bearing of these results, which are not entirely in accordance with present views as to the condition of cobalt salts in solution (compare Donnan and Bassett, Trans., 1902, **81**, 939).

Photographs of the different spectra are given in the paper.

G. S.

Compounds of Thiocarbamide and of Xanthamide with Salts of Univalent Copper. Arthur Rosenheim and Wilhelm Stadler (*Zeit. anorg. Chem.*, 1906, **49**, 1—12. Compare Abstr., 1903, i, 325; Kohlschütter, *ibid.*, 468).—In a former paper (*loc. cit.*), complex salts of the types $Cu(CH_4N_2S)X$, $Cu(CH_4N_2S)_2X$, and $Cu(CH_4N_2S)_3X$ (X = univalent anion) have been described; the results of some further experiments on the constitution of these salts are now given. It had already been observed that the electrical conductivity of salts of the last type increased abnormally on dilution; from a comparison of the conductivities of aqueous solutions of $Cu(CH_4N_2S)_3Cl$ and of the compound, $[Cu(CH_4N_2S)_2H_2O]NO_3$, described by Kohlschütter, the conclusion is drawn that the abnormal results referred to are due to hydrolysis of the tri-derivatives according to the equation $Cu(CH_4N_2S)_3X + H_2O = [Cu(CH_4N_2S)_2H_2O]X + CH_4N_2S$. Contrary to Kohlschütter's contention, the compound $Cu(CH_4N_2S)_3Cl$ is precipitated unchanged from aqueous solution by metallic chlorides; no satisfactory explanation of this behaviour has been found.

Complex salts of univalent copper with xanthamide, of the types $Cu(NH_2{\cdot}CS{\cdot}OEt)X$, $Cu(C_3H_7ONS)_2X$, and $Cu(C_3H_7ONS)_3X$ (X = halogen atom) have been obtained by interaction of the components dissolved in absolute alcohol. $Cu(C_3H_7ONS)Cl$ forms small, lustrous pyramids which melt at 126—127°; $Cu(C_3H_7ONS)_2Cl$ occurs in slender, colourless needles melting at 119°; $Cu(C_3H_7ONS)_3Cl$ forms crystalline plates melting at 111°. The corresponding *bromides* and *iodides* were also obtained in crystalline form.

With the object of throwing further light on the constitution of the xanthamide compounds, molecular weight determinations by the boiling point method were made in different solvents, but the results were not very conclusive. In benzene solution, the tri-derivatives seem to be split up into mono- or di-derivatives and the free base, whilst the di-derivatives have double the normal molecular weight. Conductivity measurements in absolute alcohol show that the mono-derivatives are most highly ionised under these conditions. G. S.

Compounds of Thiocarbamide with Salts of Bivalent Metals. Arthur Rosenheim and Victor J. Meyer (*Zeit. anorg. Chem.*, 1906, **49**, 13—27. Compare preceding abstract).—The majority of the complex salts here described were obtained by interaction of varying proportions of their components in aqueous solution. It is shown by solubility and electrical conductivity measurements that the stability of these compounds decreases in the order: Hg, Pb, Cd, Zn, Co, Ni, Fe, Mn, Ca, in approximate agreement with the theory of electro-affinity of Abegg and Bodländer.

Mercury Compounds.—$Hg(CH_4N_2S)Cl_2,\frac{1}{2}H_2O$ occurs in small, well-formed needles melting at 234°; $Hg(CH_4N_2S)_2Cl_2$ forms a microcrystalline precipitate melting at 250°; $Hg(CH_4N_2S)_4Cl_2$ separates from water in large, prismatic crystals, which decompose above 180°. $Hg(CH_4N_2S)I_2$ occurs as a yellow, microcrystalline precipitate melting at 135°; $Hg(CH_4N_2S)_2I_2$, in colourless crystals;

$$Hg(CH_4N_2S)(CN)_2,\frac{1}{2}H_2O$$

forms colourless scales which decompose above 160°;

$$Hg(CH_4N_2S)_2(CN)_2$$

forms long, colourless needles melting at 181°; $Hg(CH_4N_2S)_2(SCN)_2$ crystallises from alcohol in colourless needles.

Lead Compounds.—The *compound* $Pb(CH_4N_2S)_2Cl_2$ forms long, colourless needles; the corresponding *bromide* occurs in yellowish-white needles, and the *iodide* in deep yellow needles. The *compound* $Pb(CH_4N_2S)_4(SCN)_2$ also occurs in colourless needles. Two complex *nitrates*, $Pb_2(CH_4N_2S)_2(NO_3)_2$ and $Pb_2(CH_4N_2S)_{11}(NO_3)_4$ were also obtained; the former occurs in large, well-formed prisms, the latter in long, colourless needles.

Cadmium Compounds.—$Cd(CH_4N_2S)_2Cl_2$ occurs in long, colourless needles, $Cd(CH_4N_2S)_2(SCN)_2$ in short, yellowish-white needles, and $Cd(CH_4N_2S)_3SO_4$ in colourless prisms.

Zinc Compounds.—$Zn(CH_4N_2S)_4(NO_3)_2$ forms colourless, lustrous plates; $Zn(CH_4N_2S)_2(SCN)_2$ forms small needles; $Zn(CH_4N_2S)_3SO_4$ occurs in colourless, tabular crystals.

Cobalt Compounds.—$Co_2(CH_4N_2S)_7Cl_4$ forms bluish-black crystals; $Co(CH_4N_2S)_4(NO_3)_2$, deep bluish-green crystals; $Co(CH_4N_2S)_3(SO_4)_2$, a deep blue, crystalline powder; $Co(CH_4N_2S)_2(SCN)_2$, lustrous, brown needles.

Nickel Compounds.—$Ni_2(CH_4N_2S)_7Cl_4$ forms beautiful, yellowish-brown crystals; $Ni(CH_4N_2S)_5(NO_3)_2$, greenish-yellow prisms;

$$Ni(CH_4N_2S)_2(SCN)_2,$$

greenish-yellow needles. The cobalt and nickel compounds are relatively stable in alcohol solution, but are immediately decomposed by water.

Iron and Manganese Compounds.—$Fe(CH_4N_2S)_4Cl_2$ occurs in green crystals; $Fe(CH_4N_2S)_3(SCN)_2$ in slender, green needles;

$$Mn(CH_4N_2S)_4Cl_2$$

is obtained from an alcoholic solution in colourless, glistening plates; $Mn(CH_4N_2S)_2(SCN)_2$ forms yellowish-white, slender needles.

The only well-defined compound so far obtained with salts of the alkaline earths is $Ca(CH_4N_2S)_5Cl_2,6H_2O$; it occurs in long needles, and is completely split up into its components in aqueous solution.

G. S.

Action of Xanthates on Derivatives of Chloroacetic Acid.

HEINRICH FRERICHS and O. RENTSCHLER (*Arch. Pharm.*, 1906, **244**, 77—85).—*Sodium* benzylxanthate was prepared by treating benzyl alcohol with sodium, suspending the product in ether, and adding carbon disulphide gradually.

By heating potassium or sodium alkylxanthates, $OR\cdot CS\cdot SM$ [$R = Me, Et, Pr, CH_2Ph$; $M = K, Na$] with chloroacetylcarbamides, $CH_2Cl\cdot CO\cdot NH\cdot CO\cdot NHR'$ [$R' = H, Me$], ethyl chloroacetylcarbamate, $CH_2Cl\cdot CO\cdot NH\cdot CO\cdot OEt$, or chloroacetylarylamines, $CH_2Cl\cdot CO\cdot NR''R'''$ [$R'' : R''' = H : Ph$, $Me : Ph$, $CH_2Ph : Ph$, $H : C_6H_4Me$ *p* and *m*, $Ph : Ph$, $H : C_6H_4\cdot OMe$ *o*], in alcoholic solution, xanthylacetyl-carbamides, ethyl-carbamates, and -arylamides are obtained, of the type $OR\cdot CS\cdot S\cdot CH_2\cdot CO\cdot NH\cdot CO\cdot NHR'$, $OR\cdot CS\cdot S\cdot CH_2\cdot CO\cdot NH\cdot CO\cdot OEt$, or $OR\cdot CS\cdot S\cdot CH_2\cdot CO\cdot NR''R'''$ respectively. They are enumerated below, with their melting points.

Xanthylacetylcarbamides [$R' = H$]: *methyl-, ethyl-, propyl-, benzyl-* [$R' = Me, Et, Pr, CH_2Ph$]; 170—171°, 177—178°, 168—169°, 165° respectively. *Xanthylacetylmethylcarbamides* [$R' = Me$]: *methyl-, ethyl-, propyl-, benzyl-* [$R' = Me, Et, Pr, CH_2Ph$]; 176°, 185°, 175—176°, 189—190°.

Ethyl xanthylacetylcarbamates: *methyl-, ethyl-, propyl-* [$R = Me, Et, Pr$]; 92—93°, 103—104°, 93—94°.

Xanthylacetoanilides [$R'' : R''' = H : Ph$]: *methyl-, ethyl-, propyl-* [$R = Me, Et, Pr$]; 190—191°, 98—99°, 86—87°. *Ethylxanthylacetomethylanilide* and *-benzylanilide* [$R : R'' : R''' = Et : Me : Ph$, $Et : CH_2Ph : Ph$]; 85—86°, 65—66°. *Xanthylaceto-*p*-toluidides* [$R'' : R''' = H : C_6H_4Me$]: *methyl-, ethyl-, propyl-* [$R = Me, Et, Pr$]; 164—165°, 136°, 132—133°; *ethylxanthylaceto-*m*-toluidide*, 82°. *Ethylxanthylacetodiphenylamide* [$R : R'' : R''' = Et : Ph : Ph$], 111°. *Ethylxanthylaceto-*o*-anisidide* [$R : R'' : R''' = Et : H : C_6H_4\cdot OMe$], 53—54°. C. F. B.

Action of Ammonium Cyanide on the Saturated Ketones.

Wladimir von Gulewitsch and Th. Wasmus (*Ber.*, 1906, **39**, 1181—1194. Compare Gulewitsch, Abstr., 1900, i, 476).—Aminonitriles together with the corresponding amino-acids are formed with development of heat by the action of a small excess of ammonium cyanide on ketones of the limit series in alcoholic or alcoholic-ethereal solution (Ljubawin, Abstr., 1883, 178; Jay and Curtius, Abstr., 1894, i, 162). The best yields are obtained when the reaction takes place at the ordinary temperature for twenty hours or at 60—70° for two hours under pressure. The percentages given are those of the theoretical yields of the hydrochlorides of the aminonitriles and the copper salts of the amino-acids, in which forms the products are isolated. The aminonitriles formed from the ketones of the limit series differ from those formed from aldehydes, in that they distil without decomposing under small pressures.

α-Amino*iso*butyronitrile (compare Hellsing, Abstr., 1904, i, 563), prepared from acetone, boils at 49—50° (corr.) under 12 mm. pressure, has a sp. gr. 0·8899 at 16·9°/4°, and is readily soluble in water, alcohol, ether, or benzene; the aqueous solution turns litmus blue. The aminonitrile remains almost unchanged in a closed vessel for four months, but on exposure to air, in seven days it commences to deposit stellate aggregates of thin needles, and changes finally into a crystalline mass. When reduced with sodium and alcohol, it yields *iso*propylamine, ammonia, and hydrogen cyanide or formic acid. The *hydrochloride*, $C_4H_8N_2,HCl$ (55 per cent.), crystallises from a mixture of alcohol and ether in tetragonal or hexagonal plates, more seldom in needles, melts and decomposes at 144—146°, and has an acid reaction in aqueous solution; the *platinichloride*,

$$(C_4H_8N_2)_2,H_2PtCl_6,$$

was analysed.

α-Benzoylaminoisobutyronitrile, $NHBz{\cdot}CMe_2{\cdot}CN$, crystallises from alcohol in long, glistening needles and melts at 168·5°. *α-Amino-isobutyramide hydrochloride*, $NH_2{\cdot}CO{\cdot}CMe_2{\cdot}NH_2,HCl$, is formed when the aminonitrile hydrochloride is dissolved in fuming hydrochloric acid; it crystallises in stout prisms, becomes opaque on exposure to air, and when recrystallised from water is converted for the greater part into α-amino*iso*butyric acid, which is formed also by boiling the aminonitrile with hydrochloric acid.

The action of ammonium cyanide on methyl ethyl ketone in aqueous solution leads to the formation of α-amino-α-methylbutyric acid (Slimmer, Abstr., 1902, i, 206).

The *copper* and *nickel* salts are described.

α-Amino-α-ethylbutyronitrile hydrochloride, $CN{\cdot}CEt_2{\cdot}NH_2,HCl$ (40 per cent.), formed together with copper α-amino-α-ethylbutyrate (6 per cent.) from diethyl ketone, is obtained as a white, crystalline powder and melts at 110—113°. The *aminonitrile*, $C_6H_{12}N_2$, has a strong odour of camphor, boils at 70·8—71·7° (corr.) under 11 mm. pressure, and has a sp. gr. 0·8934 at 15·6°/4°.

α-Amino-α-methylhexonitrile hydrochloride, $C_7H_{14}N_2,HCl$ (51 per cent.), is obtained from methyl butyl ketone as a white powder, and melts at about 90—93°. The *aminonitrile*, $CH_2Pr^{\alpha}{\cdot}CMe(NH_2){\cdot}CN$, boils at 86—88° (corr.) under 10 mm. pressure, and has an odour resembling that of α-amino-α-ethylbutyronitrile. *Copper α-amino-α-methylhexoate*, $C_{14}H_{28}O_4N_2Cu.2H_2O$ (37 per cent.), crystallises in blue needles or small prisms having a violet tint.

α-Amino-α-methylisohexonitrile hydrochloride, $C_7H_{14}N_2,HCl$ (53 per cent.), formed together with the copper salt of the amino-acid (10 per cent.) from methyl *iso*butyl ketone, is obtained as a white, crystalline powder and melts at about 83—85°. The *aminonitrile*,

$$CH_2Pr^{\beta}{\cdot}CMe(NH_2){\cdot}CN,$$

boils at 74·5—76° (corr.) under 10 mm. pressure, and when reduced with sodium and alcohol yields δ-amino-β-methylpentane.

Copper α-amino-α-methylisohexoate, $C_{14}H_{28}O_4N_2Cu$, crystallises in small, light blue leaflets.

*α-Amino-α-*tert.*-butylacetonitrile hydrochloride*, $C_7H_{14}N_2,HCl$ (34 per cent.), formed together with the *copper* salt of the amino-acid (8 per cent.) from pinacolin, melts and decomposes at 155—156°.

α-Amino-α-methyloctonitrile hydrochloride, $C_9H_{18}N_2,HCl$ (55 per cent.), formed together with the copper salt of the amino-acid (29 per cent.) from methyl hexyl ketone, melts at about 104—106°.

α-Amino-α-methyloctoic acid, $C_6H_{13}{\cdot}CMe(NH_2){\cdot}CO_2H$, crystallises in small, greasy leaflets, sublimes but does not melt, and is only sparingly soluble in cold water, but is readily so in hot water or alcohol. G. Y.

Mercuric Oxycyanide. KARL HOLDERMANN (*Arch. Pharm.*, 1906, **244**, 133—136).—The molecular weight in aqueous solution, determined cryoscopically, is rather less than half that corresponding with the formula $O(Hg{\cdot}CN)_2$, although the substance is extremely little dissociated electrolytically (this vol., i, 75). As the solution has an alkaline reaction, it is probable that when the substance dissolves in water it reacts with the latter to form $2OH{\cdot}Hg{\cdot}CN$, which is slightly dissociated into the ions $\cdot OH$ and $\cdot Hg{\cdot}CN$. It gives no precipitate with silver nitrate, and therefore it can hardly form the ions $\cdot Hg{\cdot}O{\cdot}Hg\cdot$ and $2{\cdot}CN$, as suggested by Rupp (this vol., i, 340).

Mercuric oxycyanide is prepared more conveniently by the following method than by those described previously (compare Prussia, Abstr., 1899, i, 319). Dissolve 125 grams of mercuric acetate and 105 grams of mercuric cyanide in about 1 litre of nearly boiling water; filter if necessary; stir constantly, and add approximately normal aqueous sodium hydroxide until a drop of the liquid reddens phenolphthalein paper (about 800 c.c. will be required; the approach of the end-point is indicated by the sudden crystallisation of the oxycyanide). Allow to remain a day in the cold, filter, wash with cold water, and dry in the air. The mother liquor may be used once more to dissolve the same quantities of mercuric salts. C. F. B.

Constitution and Method of Formation of Trimolecular Nitriles or Cyanalkines. ERNST VON MEYER (*Chem. Centr.*, 1906, i, 941—942; from *Ber. k. Sächs. Ges. Wiss.*, **57**, 324—352. Compare Abstr., 1905, i, 155).—The paper consists for the most part of a summary of work which has already been published in reference to the trimolecular nitriles or cyanalkines, together with an account of the methods of formation and probable constitution of these compounds. *Phthalyl cyanethine*, $C_9H_{13}N_2N(CO)_2C_6H_4$, prepared by the action of phthalic acid on cyanethine, crystallises in white needles and melts at 127·5°. Unlike the alkyl derivatives, the acyl derivatives readily regenerate cyanethine. *Tribromocyanethine* forms lustrous leaflets and melts at 126°.

By the action of sodium on ethyl cyanide in ethereal solution, a solid product is formed which contains sodium cyanethine, cyanethine, sodium ethyl cyanide, and sodium cyanide; sodium propionate and ammonia are formed by secondary reactions. Ethyl cyanide yields about 60 per cent. of cyanethine, but when lithium is used instead of sodium the yield increases to 80; when potassium is used, however, it sinks to 20—25 per cent. Magnesium does not attack the cyanide except when in the active condition and at a very high temperature. When sodamide is used instead of sodium, the reduction of ethyl cyanide and the secondary reactions which result in the formation of sodium cyanide and ethane do not occur; successful experiments were made with ethyl, methyl, benzyl, and phenyl cyanides. Sodium alkyloxides, but not the phenoxide, cause polymerisation of the alkyl cyanides, especially when heated at 130—140° with the cyanide which contains the same alkyl group, a constant equilibrium between the cyanalkine, sodium alkyl cyanide, alcohol, and alkyl cyanide being probably attained. Ethyl

f f 2

cyanide is also converted into cyanethine when heated with commercial sodium cyanamide, zinc ethyl, or anhydrous barium oxide.

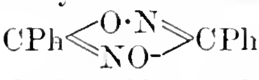
E. W. W.

Influence of the Added Substance on Substitution in Aromatic Nuclei. ARNOLD F. HOLLEMAN (*Ber.*, 1906, **39**, 1715—1716).—The partial nitration of nitrobenzene at 30° yields a mixture of 91·1 per cent. of meta-, 8·3 per cent. of ortho-, and 0·6 per per cent. of para-dinitrobenzene. The mixture obtained after complete nitration consists of 90·9 per cent. of meta-, 8·1 per cent. ortho-, and 1·0 per cent. of para-dinitrobenzene. *p*-Nitroacetanilide is the sole product of the nitration of acetanilide by dilute nitric acid; the more concentrated the acid, the greater the yield of dinitroacetanilide. The results of experiments on the nitration of nitrobenzene and of benzoic acid in the presence and absence of sulphuric acid are also quoted.

C. S.

Benzenylnitrosolic Acid. HEINRICH WIELAND and HUGO BAUER (*Ber.*, 1906, **39**, 1480—1488. Compare Wieland, Abstr., 1905, i, 420; Ley, Abstr., 1898, i, 657).—*Silver benzenylnitrosolate*, $\mathrm{NO\cdot CPh{:}N\cdot OAg,NH_3}$, is prepared by adding 8 per cent. ammonia to benzoylhydroxylaminoxime in ethereal solution, and treating the resulting solution with silver nitrate. It crystallises in unstable, matted, glistening, rose-red needles, decomposes at 94° forming ammonia, silver, benzonitrile, nitrogen peroxide, and water, detonates when heated on platinum, forms a silver mirror when boiled with water, and gives Liebermann's reaction. It is only sparingly soluble in dilute ammonia, but dissolves in moderately concentrated ammonia forming the blue *ammonium* salt, liberates iodine from potassium iodide in acid aqueous solution, and diazotises aniline in hydrochloric acid solution. The deep blue solution of the *potassium* salt is obtained when the silver salt is shaken with potassium iodide solution; with copper acetate, the ammoniacal solution forms a dark brown copper salt which rapidly decomposes, yielding an odour of benzonitrile. The free *acid* is obtained as an unstable, pale green film when the blue ammoniacal solution is treated with ether and acetic acid, and the resulting green ethereal solution is evaporated in a vacuum.

Benzenylamino-oxime, which is formed together with benzenylnitrosolic acid by the action of ammonia on benzoylhydroxylamino-oxime in ethereal solution, is obtained also by the reduction of the blue ammoniacal solution of benzenylnitrosolic acid with hydrogen sulphide.



Dibenzenyloxyazoxime, $\mathrm{CPh}\!<\!\begin{array}{c}\mathrm{O\cdot N}\\ \mathrm{NO-}\end{array}\!>\!\mathrm{CPh}$, is formed by the action of dilute nitric or hydrochloric acid on the ammoniacal solution of benzenylnitrosolic acid cooled by ice; it crystallises from petroleum in large, pale yellow, feathery plates or leaflets, melts and decomposes at 130—131°, dissolves readily in alcohol, benzene, or chloroform, gives a slight coloration with ferric chloride, and is decomposed, forming benzonitrile and benzoic and nitrous acids, when boiled with aqueous alkali hydroxides or acids; when reduced with zinc dust and glacial acetic acid in boiling alcoholic solution, it yields dibenzenylazoxime. The action of iodine on silver benzenylnitrosolate suspended in ether leads to the formation of diphenylglyoxime peroxide. G. Y.

Sulphonic Esters of Hydroxybenzaldehydes and Hydroxybenzoic Acids. Badische Anilin- & Soda-Fabrik (D.R.-P. 162322).—The esters of the formula $C_6H_4Me\cdot SO_3R$, obtained from cresols and aromatic sulphonic acids, are readily oxidised by means of manganese dioxide and sulphuric acid to the corresponding aldehydic esters, $CHO\cdot C_6H_4\cdot SO_3R$, from which the hydroxybenzaldehydes are obtained on hydrolysis.

The tolyl esters are obtained by the action of arylsulphonic chlorides on warm dilute alkaline solutions of the cresols (compare Georgescu, Abstr., 1900, i, 343). The following are the melting points:

	o-Tolyl	*p*-Tolyl	*m*-Tolyl
Benzenesulphonic	35—36°	43°	45°
p-*Toluenesulphonic*	52°	67—68°	48°
o-*Toluenesulphonic*	50—51°	70—71°	60°

The hydroxybenzaldehydesulphonic acids obtained on oxidation are crystalline compounds, insoluble in water, but dissolving in organic solvents. They yield additive compounds with sodium hydrogen sulphite, and condense with dimethylaniline and zinc chloride to form the leuco-compounds of dyes. Melting points:

	o-.	*p*-.	*m*-.
Benzenesulphonic	54—55°	82°	liquid
p-*Toluenesulphonic*	62°	73—74°	66—68°
o-*Toluenesulphonic*	79—80°	61—62°	65—66°

The corresponding carboxylic acids are obtained in small quantity at the same time.

	o-.	*p*-.	*m*-.
Benzenesulphonic ...	130°	170°	114—116°
p-*Toluenesulphonic*...	154—156°	168—170°	162°
o-*Toluenesulphonic*...	118—120°	168—170°	144—146°.

C. H. D.

Nitrostilbene. Paul Pfeiffer and J. Monath (*Ber.*, 1906, **39**, 1304—1307).—2-Nitrostilbene was prepared by a method differing slightly from that recently described by Sachs and Hilpert (this vol., i, 241). 2 : 4-Dinitrostilbene was reduced to 2-nitro-4-aminostilbene, which was diazotised in dilute hydrochloric acid solution; the properties of 2-nitrostilbene, obtained by the action of alkaline stannous chloride on the diazonium chloride, agreed with those assigned to it by Sachs and Hilpert (*loc. cit.*).

2 : 6-*Dinitrostilbene*, prepared by the condensation of 2 : 6-dinitrotoluene with benzaldehyde in the presence of a little piperidine, separates from benzene in yellow needles and melts at 86°.

2 : 4 : 6-*Trinitrostilbene*, prepared by the condensation of 2 : 4 : 6-trinitrotoluene with benzaldehyde in the presence of a little piperidine, separates from benzene in bright yellow, glistening plates or leaflets of

the *benzene additive compound*; the latter melts at 158° and loses benzene in the air. A. McK.

Triphenylmethyl. XIII. MOSES GOMBERG and LEE H. CONE (*Ber.*, 1906, **39**, 1461—1470).—Tetraphenylmethane may be readily prepared by the action of magnesium phenyl bromide on triphenylchloromethane in ethereal solution. The yield varies from 5 to 10 per cent., and other products formed are triphenylmethane and the corresponding carbinol, and triphenylmethyl peroxide.

A good yield of *αββββ-tetraphenylethane*, $CPh_3{\cdot}CH_2Ph$, is obtained by the action of magnesium benzyl chloride on triphenylchloromethane. It crystallises from a mixture of ether and light petroleum in large, transparent, monoclinic prisms, and melts at 144°. When oxidised with chromic acid, it yields triphenylcarbinol. p-*Chlorotetraphenylethane*, $C_6H_4Cl{\cdot}CPh_2{\cdot}CH_2Ph$, obtained by condensing magnesium benzyl chloride with *p*-chlorotriphenylchloromethane, melts at 156°. The corresponding 2 : 4′ : 4″-*trichloro*-derivative, $C(C_6H_4Cl)_3{\cdot}CH_2Ph$, obtained from 2 : 4′ : 4″-trichlorotriphenylchloromethane (Abstr., 1904, i, 489), melts at 140°. *Tri*-p-*bromotetraphenylethane*,

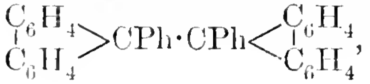
$$C(C_6H_4Br)_3{\cdot}CH_2Ph,$$

melts at 201°.

Kuntze-Fechner's *aaa*-triphenylethane (Abstr., 1903, i, 244) is obtained by condensing triphenylchloromethane with magnesium methyl iodide, and Fischer's *aaa*-triphenylpropane (*Annalen*, 1878, **194**, 261) may be prepared by a similar method.

Pentaphenylethane, $CHPh_2{\cdot}CPh_3$, may be prepared by the action of Baeyer's active magnesium (Abstr., 1905, i, 766) on a mixture of diphenylbromomethane and triphenylchloromethane in ethereal solution. It crystallises from light petroleum of high boiling point in colourless plates, begins to soften at 165°, is completely molten at 175—180°, and dissolves sparingly in ether, alcohol, or light petroleum.

Phenyl diphenylene chloromethane and molecular silver in the presence of benzene yield a *hydrocarbon*,



$$\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!\!>CPh{\cdot}CPh<\!\!\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix},$$

melting at 193°. J. J. S.

Observations on Coal Tars. ERNST BORNSTEIN (*Ber.*, 1906, **39**, 1238—1242. Compare Abstr., 1903, i, 166).—The tar obtained from a Westphalian coal has been examined. The amount formed at temperatures up to 450° is extremely small, only 9 grams per kilo. of coal. It has a sp. gr. 1·03 and contains C = 88·3, H = 7·8, and O = 2·2 per cent. It does not contain paraffins or naphthalene, but *iso*methylanthracene (Abstr., 1883, 70).

When the coal is heated to 500°, the yield of tar is 2·06 grams per 100 grams of coal, of which some 30 per cent. distils above 350°.

Another component of the tar is the hydrocarbon crackene, $C_{24}H_{18}$ (Abstr., 1900, i, 284). These two hydrocarbons appear to be characteristic of tars obtained at moderate temperatures from coals rich in carbon. J. J. S.

Pseudo-acids. HANS EULER (*Ber.*, 1906, **39**, 1607—1615. Compare Hantzsch, Abstr., 1899, i, 399; 1904, i, 381, 725; von Zawidski, 1904, i, 232, 475; Johnston, *ibid.*, i, 984).—The group of pseudo-acids discussed comprises the compounds which exhibit neither slow neutralisation nor abnormal hydrolysis, for example, phenylnitroamine and violuric acid. Electrical conductivity determinations gave the following results for $K \times 10^6$ at 18°:

	Water.	41 per cent. alcohol.
Phenylnitroamine	17·5	1·26
Acetic acid	17·8	1·86

The temperature-coefficient for K is somewhat larger than that for acetic and benzoic acids and their homologues and increases with the temperature, but only to somewhat the same extent as for other feeble electrolytes, such as phenol and aniline, and for nitrogen acids such as aminotetrazole. The behaviour of phenylnitroamine towards ammonia in perfectly dry benzene solution is quite analogous to that of benzoic acid, and the conclusion is drawn that so far no physico-chemical proofs of molecular rearrangement of phenylnitroamine during ionisation or salt formation are available.

Conductivity determinations of solutions of aniline acetate and aniline violurate indicate that the two salts are hydrolysed to much the same extent, and the two acids have dissociation constants of much the same value. If a solution of violuric acid contains 99 per cent. of non-ionised pseudo-acid as stated by Hantzsch, then it is calculated that the true acid is twice as strong as monochloroacetic acid.

J. J. S.

Acylation of Anilinesulphonic Acids. GEORG SCHROETER [with GEORG RÖSING] (*Ber.*, 1906, **39**, 1559—1570).—Finely-powdered dry sodium sulphanilate and acetic anhydride interact with development of heat to form sodium acetylaniline-*p*-sulphonate (Nietzki and Benckiser, Abstr., 1884, 1024), which is readily soluble in water, but is only sparingly so in alcohol, and has no physiological action. The acid $NHAc\cdot C_6H_4\cdot SO_3H$ (Armstrong, *Proc.*, 1899, **15**, 177; Junghahn, Abstr., 1900, i, 389) is obtained in slender needles on addition of concentrated hydrochloric acid to the cold concentrated aqueous solution of the sodium salt; it separates from a mixture of alcohol and ether as an oil, which solidifies to a powder containing $2H_2O$, is readily soluble in water or alcohol, but is insoluble in concentrated hydrochloric acid, and is hydrolysed only slowly when boiled with water, but more rapidly by boiling alcohol, forming sulphanilic acid and acetic acid and ethyl acetate respectively.

Acetylaniline-p-*sulphonyl chloride*, $NHAc\cdot C_6H_4\cdot SO_2Cl$, is formed when sodium acetyl-*p*-anilinesulphonate is ground with phosphorus pentachloride and treated with cold water; it crystallises from benzene in small needles, melts at 149°, is readily soluble in alcohol, ether, or ethyl acetate, and reacts with sodium ethoxide in alcoholic solution to form *ethyl acetylaniline*-p-*sulphonate*, $NHAc\cdot C_6H_4\cdot SO_3Et$, which crystallises in white needles and melts at 115°. *Acetylaniline-*

p-*sulphonylphenetidide*, $NHAc\cdot C_6H_4\cdot SO_2\cdot NH\cdot C_6H_4\cdot OEt$, formed by the action of the sulphonyl chloride on phenetidine, crystallises from aqueous solution in glistening, white leaflets and melts at 204°.

Sodium acetylnaphthionate, $C_{12}H_{10}O_4NSNa$, prepared by treating sodium naphthionate with acetic anhydride, is obtained as a white powder, which is soluble in water, but only sparingly so in alcohol. Acetylnaphthionic acid, $NHAc\cdot C_{10}H_6\cdot SO_3H,\frac{1}{2}H_2O$, crystallises in needles, is insoluble in concentrated hydrochloric acid, and when boiled with water is hydrolysed to acetic and naphthionic acids. *Acetylnaphthionyl chloride*, $NHAc\cdot C_{10}H_6\cdot SO_2Cl$, prepared by grinding the dry sodium salt with phosphorus pentachloride, separates from ethyl acetate in transparent crystals and decomposes, but does not melt, when heated. *Ethyl acetylnaphthionate*, $NHAc\cdot C_{10}H_6\cdot SO_3Et$, crystallises from benzene in white needles and melts at 148°. The *anilide*, $NHAc\cdot C_{10}H_6\cdot SO_2\cdot NHPh$, crystallises from alcohol in leaflets and melts at 231°.

Sodium 5-acetylaminonaphthalene-1-sulphonate, $NHAc\cdot C_{10}H_6\cdot SO_3Na$, is formed by heating sodium 5-aminonaphthalene-1-sulphonate with acetic anhydride; when treated with phosphorus pentachloride, it yields 5-*acetylaminonaphthalene*-1-*sulphonyl chloride*,

$$NHAc\cdot C_{10}H_6\cdot SO_2Cl.$$

Sodium benzoylaniline-p-*sulphonate*, $NHBz\cdot C_6H_4\cdot SO_3Na$, formed by shaking sodium sulphanilate with benzoyl chloride and sodium hydroxide in aqueous solution, crystallises in white needles, and, when ground with phosphorus pentachloride, yields *benzoylaniline*-p-*sulphonyl chloride*, $NHBz\cdot C_6H_4\cdot SO_2Cl$, which crystallises in yellow needles and melts at 176°.

Sodium benzoylnaphthionate, $NHBz\cdot C_{10}H_6\cdot SO_3Na$, is formed by heating sodium naphthionate with benzoic anhydride.

Sodium benzenesulphonylaniline-p-*sulphonate*, $C_{12}H_{10}O_5NS_2Na$, is formed by shaking sodium sulphanilate with benzenesulphonyl chloride and aqueous sodium hydroxide. The *acid*, $SO_2Ph\cdot NH\cdot C_6H_4\cdot SO_3H$, forms an oil, which crystallises and melts at 78°. The *chloride*, $SO_2Ph\cdot NH\cdot C_6H_4\cdot SO_2Cl$, crystallises in white needles and melts at 177°.

Sodium benzenesulphonylnaphthionate, $C_{16}H_{12}O_5NS_2Na$, prepared in the same manner from sodium naphthionate, crystallises from alcohol in leaflets. The free *acid*, $SO_2Ph\cdot NH\cdot C_{10}H_6\cdot SO_3H$, crystallises in needles. The *sulphonyl chloride*, $SO_2Ph\cdot NH\cdot C_{10}H_6\cdot SO_2Cl$, crystallises from benzene and melts at 171°.

Sodium acetylnaphthionate reacts with diazotised bases in aqueous solution to form diazonium salts, $NHAc\cdot C_{10}H_6\cdot SO_3\cdot N_2\cdot Ar$, which may be recrystallised from moderately hot water, are soluble in aqueous sodium hydroxide, give dark violet precipitates with ammonia in aqueous solution, detonate when heated on platinum, decompose and evolve nitrogen when boiled with water, and crystallise as follows.

With α-naphthylamine: crystallises in yellowish-brown, glistening, silky leaflets; with diazotised *o*- or *p*-nitroaniline: dark red, glistening needles; with diazotised *m*-nitroaniline: light yellowish-red leaflets; with diazotised benzidine: glistening, red needles.

Similar *diazonium* salts are obtained by the action of sodium

5-acetylaminonaphthalene-1-sulphonate on diazotised *p*-nitroaniline, crystallising in reddish-brown, and on diazotised benzidine, crystallising in yellowish-brown leaflets.

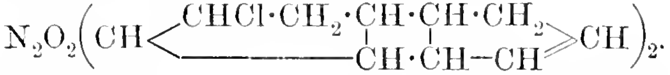
In aqueous solution, sodium benzenesulphonylaniline-*p*-sulphonate reacts with diazotised benzidine to form a yellowish-brown *diazonium* salt, $C_{36}H_{28}O_{10}N_6S_4$, which chars when heated, and gives a violet-black precipitate with ammonia; with diazotised *o*-nitroaniline to form the *diazonium* salt, $C_{18}H_{14}O_7N_4S_2$, which crystallises in orange-yellow needles and forms a red solution in aqueous sodium hydroxide; with diazotised *m*-nitroaniline to form the yellow *powder*, $C_{18}H_{14}O_7N_4S_2$, which dissolves to a red solution in aqueous sodium hydroxide, and with diazotised *a*-naphthylamine and *ψ*-cumidine to form similar diazonium salts. It couples with diazotised *p*-nitroaniline, forming the *azo*-dye, $C_{18}H_{14}O_7N_4S_2$, which crystallises in reddish-yellow needles, dissolves in aqueous sodium hydroxide or ammonia, forming a red solution, does not evolve nitrogen when boiled with water, and dyes wool yellow in an acid solution.

In aqueous solution, sodium benzenesulphonylnaphthionate reacts with diazotised benzidine to form the *diazonium* salt, $C_{44}H_{32}O_{10}N_6S_4$, which is obtained as a yellow powder, and with diazotised *m*-nitroaniline to form the yellow *diazonium* salt, $C_{22}H_{16}O_7N_4S_2$. With diazotised *p*-nitroaniline, sodium benzenesulphonylnaphthionate forms the *azo*-dye, $C_{22}H_{16}O_7N_4S_2$, which crystallises in red needles, does not evolve nitrogen when boiled with water, and dyes wool orange.

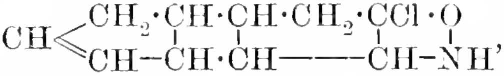
When cotton-wool is boiled with benzenesulphonylaniline-*p*-sulphonyl chloride in chloroform solution in presence of pyridine, washed, and treated with *p*-nitrophenyldiazonium acetate, the fibres are dyed yellow.

Mercerised cotton-wool is dyed orange-brown when boiled with benzenesulphonylnaphthionyl chloride in chloroform solution, washed, and treated with *p*-nitrophenyldiazonium solution. G. Y.

Di*cyclo*pentadienes. I. Heinrich Wieland (*Ber.*, 1906, **39**, 1492—1499).—Krämer and Spilker's di*cyclo*pentadiene nitrosochloride (Abstr., 1896, i, 289) has the constitution

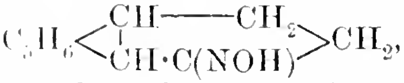


$$N_2O_2\left(CH<\begin{matrix}CHCl\cdot CH_2\cdot CH\cdot CH\cdot CH_2\\ \overline{\qquad\qquad\quad} CH\cdot CH-CH\end{matrix}>CH\right)_2.$$



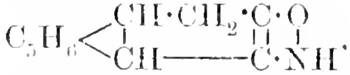
When heated with diethylaniline at 140°, it is converted into the *mononitrosochloride*, $CH<\begin{matrix}CH_2\cdot CH\cdot CH\cdot CH_2\cdot CCl\cdot O\\ CH-CH\cdot CH\text{———}CH-NH\end{matrix}$, which crystallises from alcohol in hard, colourless plates, melts and commences to decompose at 160°, and is readily soluble in most solvents.

The *quinolinium chloride*, $OH\cdot N\colon C_{10}H_{11}\cdot C_9NH_7Cl$, which crystallises in colourless needles and decomposes at 270°, and the *pyridinium chloride*, $OH\cdot N\colon C_{10}H_{11}\cdot C_5NH_5Cl$, which melts and decomposes at 218°, and forms a *platinichloride* crystallising in stellate aggregates of orange needles and blackening at 205°, are obtained by heating Krämer and Spilker's nitrosochloride with quinoline and pyridine respectively.

When reduced with zinc dust and glacial acetic acid in methyl alcoholic solution, the mononitrosochloride forms the *oxime* of ketodihydrodi*cyclo*pentadiene,  $C_5H_6<\begin{array}{l}CH\text{——}CH_2\\ \vert \\ CH\cdot C(NOH)\end{array}>CH_2$, which crystallises in large, fan-shaped crystals, melts at 88°, is readily soluble in most solvents, and when boiled with dilute sulphuric acid yields an aromatic oil with a nitrile-like odour.

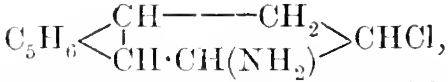
*Aminodihydro*cyclo*dipentadiene,*  $C_5H_6<\begin{array}{l}CH\text{——}CH_2\\ \vert \\ CH\cdot CH(NH_2)\end{array}>CH_2$, is formed together with the oxime by the reduction of the nitrosochloride or by reduction of the oxime with zinc dust and hydrochloric acid; the *hydrochloride* crystallises in glistening prisms and melts at 198°; the *picrate* forms matted, yellow needles and melts and blackens at 193°.

The action of alcoholic potassium hydroxide on the mononitrosochloride leads to the formation of the *ψ oxime*,



$$C_5H_6<\begin{array}{l}CH\cdot CH_2\cdot C\cdot O\\ \vert \qquad\quad\;\; \Vert \quad \vert \\ CH\text{———}C\cdot NH\end{array},$$

which melts and decomposes at 205° and is insoluble in alkali hydroxides.

*Chloroaminodihydrodi*cyclo*pentadiene,*  $C_5H_6<\begin{array}{l}CH\text{——}CH_2\\ \vert \\ CH\cdot CH(NH_2)\end{array}>CHCl$, is prepared by reduction of Krämer and Spilker's nitrosochloride with granulated zinc and boiling alcoholic hydrochloric acid; it is obtained as an oil with a strong, repulsive odour. The *hydrochloride,* $C_{10}H_{15}NCl_2$, crystallises in stout, glistening plates, commences to melt and decompose at 260°, and when treated with sodium nitrite and hydrochloric acid yields the corresponding volatile *alcohol*. The *platinichloride,* $(C_{10}H_{11}NCl)_2,H_2PtCl_6$, crystallises in stellate aggregates of yellowish-brown needles and melts and decomposes at 205°; the *picrate,* $C_{16}H_{18}O_7N_4Cl$, forms glistening, greenish-yellow needles and decomposes at 228°.
G. Y.

Dipropylacetyl-*p*-phenetidine. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 163034).—*Dipropylacetyl-p-phenetidine,* $CHPr_2\cdot CO\cdot NH\cdot C_6H_4\cdot OEt$, prepared by boiling α-propylvaleric acid and *p*-phenetidine in a reflux apparatus, crystallises from benzene, melts at 147°, and dissolves sparingly in hot water, readily in hot alcohol or benzene. It finds therapeutic application as a substitute for antipyrine.
C. H. D.

Action of Primary Amines on Aldehydes. LEOPOLD RUGHEIMER (*Ber.*, 1906, **39**, 1653—1664).—Compounds of the type $CCl_3\cdot CH(NH\cdot R)_2$, formed from chloral and aromatic amines, are sufficiently stable to permit of being directly nitrated. When *p*-ditoluidinetrichloroethane, $CCl_3\cdot CH(NH\cdot C_6H_4Me)_2$, for example, is added to a mixture of anhydrous nitric acid and glacial acetic acid, it is nitrated, and, when the product is poured into water, chloral separates, whilst *m*-nitro-*p*-toluidine can also be obtained by saturating the solution with sodium carbonate. Compounds of the type $CCl_3\cdot CH(OH)\cdot NHR$, described in the paper, do not, however, behave in an analogous manner.

The mechanism of the interaction between primary amines and aldehydes is discussed.

Chloral-o-*phenylenediamine*, $CCl_3\cdot CH(OH)\cdot NH\cdot C_6H_4\cdot NH_2$, prepared by the addition of a solution of chloral in light petroleum to a solution of *o*-phenylenediamine in ether, is a colourless solid melting at about 72°. When the compound is added to sulphuric acid at $-6°$, the odour of chloral is perceptible. Diacetyl-*o*-phenylenediamine is formed by the action of acetic anhydride.

Chloral-p-*phenylenediamine*, prepared in an analogous manner, decomposes at about 80°.

Chloral-1 : 2 : 4-*tolylenediamine*, $CCl_3\cdot CH(OH)\cdot NH\cdot C_6H_3Me\cdot NH_2$, melts at about 86°.

Chloral-1 : 3 : 4 *tolylenediamine* melts at 67—68°. Its *mercurichloride* separates from chloroform in needles and decomposes at about 120°.

Dichloral-1 : 3 : 4-*tolylenediamine*, $C_6H_3Me[NH\cdot CH(OH)\cdot CCl_3]_2$, melts at 56—57°.

Chloral-a-*naphthylamine*, $CCl_3\cdot CH(OH)\cdot NH\cdot C_{10}H_7$, prepared from chloral and *α*-naphthylamine, crystallises in needles and melts at 93—93·5°. It forms acetonaphthalide when acted on by acetic anhydride.

Chloral-*β*-*naphthylamine* separates from light petroleum in needles and melts at 101°.

Chloral-aniline chloral hydrate, $CCl_3\cdot CH(OH)\cdot NHPh,CCl_3\cdot CH(OH)_2$, prepared by the addition of a solution of chloral in light petroleum to a solution of aniline in ether, separates in needles, grouped in rosettes, and melts at 56·5°.

Chloral-p-*toluidine chloral hydrate*,

$$CCl_3\cdot CH(OH)\cdot NH\cdot C_6H_4Me,CCl_3\cdot CH(OH)_2,$$

melts at 58—59·5°. A. McK.

Rate of Auto-racemisation of Optically Active Ammonium Salts. Edgar Wedekind (*Zeit. Elektrochem.*, 1906, **12**, 330—333).—The velocity of the spontaneous change of *d*-phenylbenzylmethylpropylammonium iodide into the racemic form in chloroform solution at 25° is measured. The reaction appears to be unimolecular, which is in accordance with the view that the change is due to the dissociation of the salt into the substituted ammonia and alkyl iodide, which subsequently recombine to the racemic form. T. E.

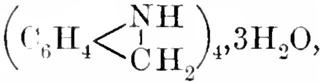
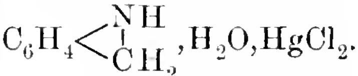
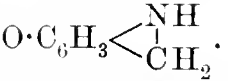
Chlorophenylcarbamides. Richard Doht (*Monatsh.*, 1906, **27**, 213—223. Compare Abstr., 1905, i, 49).—o-*Chlorophenylcarbamide*, $NH_2\cdot CO\cdot NH\cdot C_6H_4Cl$, formed by the action of potassium cyanate on *o*-chloroaniline, crystallises in thin, doubly refracting, monoclinic prisms, melts at 152° (corr.), and is soluble in water, alcohol, or acetone.

m-*Chlorophenylcarbamide*, prepared from *m*-chloroaniline, crystallises in large, pointed, doubly refracting needles and melts at 142° (corr.).

p-*Chlorophenylcarbamide* is formed by the action of potassium cyanate on *p*-chloroaniline, or of 1 mol. of chlorine or of bleaching powder equivalent to 1 mol. of chlorine on phenylcarbamide in acetic acid solution; it crystallises in doubly refracting prisms and melts at 204—207° (corr.).

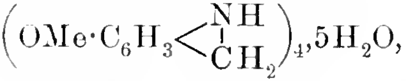
2 : 4-*Dichlorophenylcarbamide*, $NH_2·CO·NH·C_6H_3Cl_2$, is formed by the action of an excess of chlorine, or of bleaching powder equivalent to not less than 2 mols. of chlorine, on phenylcarbamide in acetic acid solution; it crystallises in sheaves of broad needles, melts at 189° (corr.), and when boiled with acetic anhydride yields 2 : 4-dichloroacetanilide, melting at 143°.

The action of chlorine on phenylcarbamide in hot glacial acetic acid solution leads to the formation of 2 : 4 : 6-trichloroacetanilide, ammonium chloride, and carbon dioxide. G. Y.

New Synthesis of Benzyleneimide. E. I. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 1272—1277).—The author has synthesised benzyleneimide by the interaction of aniline and formaldehyde in presence of tartaric or citric acid. The yellow base, to which, when dried at 100°, the author ascribes the formula  $\left(C_6H_4<\begin{smallmatrix}NH\\ \vert\\ CH_2\end{smallmatrix}\right)_4,3H_2O$, is soluble in dilute or concentrated acetic acid and dissolves sparingly in chloroform. The addition of sodium nitrite to a solution of the imide in acetic or a mineral acid yields the corresponding *iso*nitroso-compound, which readily forms colouring matters with alkaline β-naphthol or similar compounds. For technical purposes, it is not necessary to isolate the base in order to introduce the nitroso-compound, the original acetic acid compound being employed. The addition of excess of mercuric chloride to an acetic acid solution of the imide precipitates a yellow *compound*,  $C_6H_4<\begin{smallmatrix}NH\\ \vert\\ CH_2\end{smallmatrix},H_2O,HgCl_2$. When kept, an acetic acid solution of the *iso*nitroso-compound deposits an orange precipitate of the nitroso-compound,  $NO·C_6H_3<\begin{smallmatrix}NH\\ \vert\\ CH_2\end{smallmatrix}$.

Benzyleneimide can also be synthesised by first preparing anhydroformaldehydeaniline and then heating this with tartaric and acetic acids.

The following imides have also been prepared:

(1)  $\left(OMe·C_6H_3<\begin{smallmatrix}NH\\ \vert\\ CH_2\end{smallmatrix}\right)_4,5H_2O$,

from *o*-anisidine, is an amorphous powder melting at above 100°; (2)  $C_6H_3Me<\begin{smallmatrix}NH\\ \vert\\ CH_2\end{smallmatrix},3H_2O$, from *o*-toluidine, resembles the preceding and melts at above 100°. (3) The imide from *p*-toluidine is a soft resin which solidifies on standing. T. H. P.

Constitution and Colour of Nitrophenols. GEORG VON GEORGIEVICS (*Ber.*, 1906, **39**, 1536—1538. Compare Hantzsch, this vol., i, 353).—Aqueous and alcoholic solutions of picric acid darken when heated, regaining the original colour on cooling. Wool is dyed a lighter shade in a cold than in a hot picric acid bath; on prolonged boiling with water, the wool dyed in the cold darkens to the shade of that dyed in the hot bath. If picric acid is exposed to the air in a thin layer, it darkens in colour, and if treated with benzene is separated into the ordinary yellow, soluble picric acid and a dark modification which is almost insoluble in benzene, becomes still darker above 200°, and does not melt at 230°. G. Y.

Catalytic Action of the Alkali and Alkaline-earth Salts in the Fixation of Atmospheric Oxygen by Solutions of the Polyphenols. E. Fouard (*Compt. rend.*, 1906, **142**, 796—798).—The halogen salts of the alkali and alkaline-earth metals exert a catalytic action on the absorption of oxygen by solutions of guaiacol or quinol. If to equal volumes of $2N$ solutions of the chlorides of the metals a definite quantity of a guaiacol solution is added, the time (t) required for each solution to attain a definite blue tint varies inversely with the equivalent (v) of the metal; the curve representing the relation between t and v is hyperbolic, and expressed by the equation $tv^x =$ constant. The amount of oxygen absorbed in a given time by a definite quantity of quinol in the presence of equal volumes of $2N$ solutions of the metallic chlorides is greatest in the case of sodium, and then follow, in decreasing order of activity, manganese, calcium, potassium, barium, lithium, and strontium. M. A. W.

Derivatives of Catechol Methylene Ether. Paul Medinger (*Monatsh.*, 1906, **27**, 237—246).—*Homopiperonylonitrile*,

$$CH_2:O_2:C_6H_3\cdot CH_2\cdot CN,$$

is formed by boiling the oxime of homopiperonaldehyde (Bouveault and Wahl, Abstr., 1902, i, 682) with acetic anhydride in a reflux apparatus for thirty minutes; it is obtained as a yellow oil, which distils at 159° under 14 mm. pressure, solidifies to compact, white crystals melting at 42°, and is hydrolysed to homopiperonylic acid when boiled with alcoholic potassium hydroxide. The *acetyl* derivative of homopiperonaldoxime, $CH_2:O_2:C_6H_3\cdot CH_2\cdot CH:N\cdot OAc$, is formed together with the nitrile when the oxime is boiled with acetic anhydride for fifteen minutes; it distils at 177° under 14 mm. pressure, solidifies to white crystals melting at 96°, and on prolonged heating in a reflux apparatus decomposes, forming acetic acid and the nitrile.

Homopiperonylamine, $CH_2:O_2:C_6H_3\cdot CH_2\cdot CH_2\cdot NH_2$, prepared by reducing the oxime of homopiperonaldehyde with sodium and alcohol, is obtained as a colourless oil, which boils at 145° under 17 mm. pressure; the colourless, crystalline *hydrochloride*, $C_9H_{11}O_2N,HCl$, melts at 197° and is readily soluble in water.

Homopiperonyl alcohol, $CH_2:O_2:C_6H_3\cdot CH_2\cdot CH_2\cdot OH$, formed by the action of silver nitrite on the hydrochloride of the amine in aqueous solution, is obtained as an almost colourless, strongly refracting oil with a pleasant aromatic odour, which boils at 164° under 18 mm. pressure. G. Y.

o-o-Dihydroxydiphenyl Sulphide. Ferdinand Mauthner (*Ber.*, 1906, **39**, 1347—1351).—Thioguaiacol was prepared from *o*-anisidine by Leuckart's diazo-reaction, whilst *thioguaiacol xanthate* was obtained as a by-product; the latter separates from alcohol in colourless leaflets and melts at 123°. Thioguaiacol was converted into its sodium salt, which was condensed with *o*-iodoanisole in the presence of copper as a catalyst to form o-o-*dimethoxydiphenyl sulphide*, $C_{14}H_{14}O_2S$, which separates from alcohol in colourless leaflets, melts at 73°, and boils at 252—253° under 10 mm. pressure. Its solution in concentrated sulphuric acid is blue, and becomes colourless on the addition of water.

o-o-*Dimethoxydiphenylsulphone*, prepared by the oxidation of the sulphide by potassium permanganate, crystallises from benzene in colourless needles and melts at 157—158°. Its solution in concentrated sulphuric acid becomes blue on warming, but loses this tint when diluted with water.

When *o-o*-dimethoxydiphenyl sulphide in xylene solution is warmed for two hours with aluminium chloride, o-o-*dihydroxydiphenyl sulphide*, $C_{12}H_{10}O_2S$, may be isolated from the product; it separates from benzene in colourless needles and melts at 142°. Its solution in sulphuric acid is bright green, but this tint disappears when the solution is diluted. In aqueous solution it gives a green coloration with ferric chloride. Its *acetyl* derivative separates from alcohol in colourless needles and melts at 95—96°. *Acetyl* o-o-*dihydroxydiphenylsulphone*, $C_{16}H_{14}O_6S$, prepared by oxidising *o-o*-diacetyldihydroxydiphenyl sulphide in glacial acetic acid solution with potassium permanganate, separates from alcohol in colourless needles and melts indefinitely at 147—148°. It forms a blue solution with concentrated sulphuric acid. When treated with sodium hydroxide and the solution then acidified, the acetyl compound forms o-o-*dihydroxydiphenylsulphone*, $C_{12}H_{10}O_4S$, which separates from benzene in colourless needles and melts at 164—165°. Its solution in sulphuric acid is blue, and becomes colourless on dilution with water. A. McK.

Conversion of Morphenol into Trihydroxyphenanthrene.

EDUARD VONGERICHTEN and O. DITTMER (*Ber.*, 1906, **39**, 1718—1722). —3 : 4 : 5-*Trihydroxyphenanthrene*, $C_{14}H_{10}O_3$, is obtained when morphenol is heated with potassium hydroxide at 250°; after purification, it separates from water in glassy leaflets, softens at 120°, and melts at 148°. When heated in methyl-alcoholic solution with methyl iodide and sodium methoxide, it yields 3 : 4 : 5-*trimethoxyphenanthrene*, $C_{17}H_{16}O_3$, which melts at 90°. The *picrate* melts at 166°. The triacetyl derivative, which could not be obtained in the crystalline state, is readily oxidised by chromic and glacial acetic acids to a quinone which dissolves in alcoholic soda to a red solution, quickly changing to violet, and forms with *o*-tolylenediamine a yellow, crystalline azine. The compound of the quinone with sodium hydrogen sulphite is decomposed by sulphuric acid, yielding a quinone which dissolves in alcoholic soda to an intensely violet solution.

C. S.

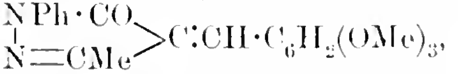
Condensation Products of Asaryl Aldehyde.

RUDOLF FABINYI and TIBOR SZÉKI (*Ber.*, 1906, **39**, 1211—1218. Compare Butleroff and Rizza, Abstr., 1885, 669; Gattermann and Eggers, Abstr., 1899, i, 347).—2 : 4 : 5-*Trimethoxybenzylidene semicarbazide*, $C_6H_2(OMe)_3\cdot CH:N\cdot NH\cdot CO\cdot NH_2$, crystallises from alcohol in small, white needles and melts at 205—206°.

2 : 4 : 5-*Trimethoxybenzylidene-β-naphthylamine*, $C_6H_2(OMe)_3\cdot CH{:}N\cdot C_{10}H_7$, crystallises from alcohol in yellow leaflets and melts at 134° ; the *hydrochloride*, $C_{20}H_{19}O_3N,HCl$, forms glistening, red, rhombic crystals with blue lustre and dissolves in water to a yellow solution.

2 : 2′ : 4 : 4′ : 5 : 5′-*Hexamethoxydibenzylidenebenzidine*, $C_{32}H_{32}O_6N_2$, crystallises in slender needles and is readily soluble in chloroform or benzene, but only sparingly so in alcohol or ether ; the *hydrochloride*, $C_{32}H_{32}O_6N_2,2HCl$, forms slender, red, microscopic needles.

1-Phenyl-4(2′ : 4′ : 5′)-trimethoxybenzylidene-3-methyl-5-pyrazolone,



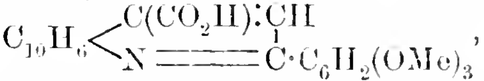
$\begin{matrix}NPh\cdot CO\\ N{=}CMe\end{matrix}{>}C{:}CH\cdot C_6H_2(OMe)_3$, formed by the action of the aldehyde on phenylmethylpyrazolone in alcoholic solution at the ordinary temperature, crystallises in long, slender, glistening, orange-red needles and melts at 230°.

2 : 4 : 5-*Trimethoxybenzylideneacetone*, $C_6H_2(OMe)_3\cdot CH{:}CH\cdot COMe$, formed by the interaction of asaryl aldehyde and acetone in presence of sodium hydroxide in warm alcoholic solution, crystallises in delicate, orange-yellow leaflets, melts at 173°, and gives with concentrated sulphuric acid a cherry-red, and with bromine in chloroform solution a greenish-blue, coloration, becoming yellow on addition of an excess of bromine. With bromine in carbon disulphide solution, it forms a yellow, crystalline *dibromide* (?). The *di-iodide*, $C_6H_2(OMe)_3\cdot CHI\cdot CHI\cdot COMe$, formed by the action of iodine on trimethoxybenzylideneacetone in warm alcoholic solution, separates in glistening, metallic, dark bluish-green, woolly crystals, and is decomposed into iodine and trimethoxybenzylideneacetone when boiled with water. The *oxonium hydrochloride*, $C_{13}H_{16}O_4,HCl$, is formed by the action of hydrogen chloride on trimethoxybenzylideneacetone in absolute alcoholic solution ; it separates in bluish-green, woolly crystals with metallic lustre, and is unstable. 2 : 4 : 5-*Trimethoxybenzylidenemethyl ethyl ketone*, $C_6H_2(OMe)_3\cdot CH{:}CH\cdot COEt$, formed by the condensation of trimethoxybenzaldehyde with methyl ethyl ketone in presence of sodium hydroxide in aqueous-alcoholic solution, separates in light yellow crystals, melts at 155°, and gives an intense red coloration with bromine in chloroform solution.

2 : 4 : 5-*Trimethoxybenzylidenemethyl propyl ketone*, $C_6H_2(OMe)_3\cdot CH{:}CH\cdot COPr^a$, crystallises in yellow needles and melts at 87°.

2 : 4 : 5-*Trimethoxybenzylidenediacetophenone*, $C_6H_2(OMe)_3\cdot CH(CH_2\cdot COPh)_2$, crystallises from alcohol in slender, white needles and melts at 119—120°. The oxime, $C_{26}H_{28}O_5N_2$, forms white needles and melts at 167—168°.

2(2′ : 4′ : 5′)-*Trimethoxyphenyl-β-naphthacinchonic acid*,



$$C_{10}H_6{<}\begin{matrix}C(CO_2H){:}CH\\ N{=\!=\!=}C\cdot C_6H_2(OMe)_3\end{matrix},$$

is prepared by heating 2 : 4 : 5-trimethoxybenzaldehyde with β-naphthylamine and pyruvic acid in absolute alcoholic solution in a reflux apparatus; it crystallises in matted, slender, yellow needles, melts at 258°, and is insoluble in the ordinary solvents.

2 : 4 : 5-*Trimethoxy-α-phenylcinnamonitrile*,

$$C_6H_2(OMe)_3\cdot CH{:}CPh\cdot CN,$$

formed by condensation of trimethoxybenzaldehyde with benzyl cyanide, crystallises in yellowish-green needles and melts at 147—148°. G. Y.

Action of Magnesium Organic Compounds on Asaryl Aldehyde. Rudolf Fabinyi and Tibor Széki (*Ber.*, 1906, **39**, 1218—1222).—*Diphenyldi-*2 : 4 : 5-*trimethoxyphenylmethyl ether*,

$$O[CHPh\cdot C_6H_2(OMe)_3]_2,$$

is formed by the action of magnesium phenyl iodide on asaryl aldehyde in benzene-ethereal solution; it crystallises in delicate, colourless leaflets or needles, melts at 210°, is readily soluble in hot benzene, glacial acetic acid, or chloroform, and gives with concentrated sulphuric acid an intense red and with concentrated hydrochloric acid a red coloration changing to blue.

γδ-*Di*-2 : 4 : 5-*trimethoxyphenyl*-Δ^{β}-*hexene*,

$$C_6H_2(OMe)_3\cdot CHEt\cdot C(CHMe)\cdot C_6H_2(OMe)_3,$$

is formed by the action of magnesium ethyl iodide on asaryl aldehyde in benzene-ethereal solution; it crystallises from alcohol in small, white leaflets, melts at 96°, dissolves in concentrated sulphuric acid forming a yellowish-red solution, and gives with concentrated hydrochloric acid a red coloration changing to blue. When heated with bromine in carbon disulphide solution, it forms the *dibromide*,

$$C_{24}H_{32}O_6Br_2,$$

which crystallises in small, white needles, gradually becomes grey, and melts and decomposes at 104—106°.

Di-2 : 4 : 5-*trimethoxy-α-phenyl ethyl ether*, $O[CHMe\cdot C_6H_2(OMe)_3]_2$, formed by the action of magnesium methyl iodide on asaryl aldehyde, crystallises from alcohol and melts at 111·5°. G. Y.

Monohalogen Derivatives of Triphenylcarbinol Chloride [Triphenylchloromethane]. Lee H. Cone and C. P. Long (*J. Amer. Chem. Soc.*, 1906, **28**, 518—524).—*p*-Bromotriphenylchloromethane (Gomberg, Abstr., 1904, i, 489) can be prepared by the action of hydrogen chloride on the carbinol obtained by the reaction between magnesium phenyl bromide and methyl *p*-bromobenzoate or *p*-bromobenzophenone.

p-*Bromotriphenylcarbinol*, $C_6H_4Br\cdot CPh_2\cdot OH$, obtained by heating *p*-bromotriphenylchloromethane with a mixture of glacial acetic and sulphuric acids, forms colourless crystals and melts at 74°. p-*Bromotriphenylmethyl peroxide*, $O_2(CPh_2\cdot C_6H_4Br)_2$, crystallises from ether or light petroleum and melts at 171·5—173·5°. p-*Bromotriphenylmethylamine*, $C_6H_4Br\cdot CPh_2\cdot NH_2$, is a crystalline substance which melts at 108·5—109°. p-*Bromotriphenylmethylaniline* melts at 148°.

p-Bromobenzophenone can be obtained in nearly quantitative yield by the action of benzoyl chloride on bromobenzene in presence of aluminium chloride. On attempting to prepare *p*-bromotriphenylchloromethane by the action of benzene on the product of the reaction between phosphorus pentachloride and *p*-bromobenzophenone, a mixture of *p*-bromo- and *p*-chloro-triphenylchloromethanes was obtained. This result was found to be due to the fact that the product obtained by the action of phosphorus pentachloride on *p*-bromobenzophenone was not the dichloride expected but a mixture of *p*-chloro- and *p*-bromo-benzophenones.

m-*Bromotriphenylchloromethane*, prepared by Grignard's reaction from ethyl *m*-bromobenzoate, melts at 67°. E. G.

Hydrogenisation of Cholesterol. OTTO DIELS and EMIL ABDERHALDEN (*Ber.*, 1906, **39**, 1371—1373).—A reply to Neuberg (this vol., i, 356).

α-Cholestanol (this vol., i, 272) cannot be identical with coprosterol (Bondzynski, Abstr., 1896, ii, 319), as the two compounds differ in melting point, solubility, and in the characteristics of the benzoyl derivatives. C. S.

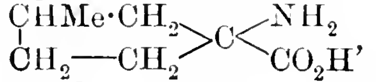
A Simple General Method for the Synthesis of α-Amino-acids. NICOLAI ZELINSKY and GEORGE STADNIKOFF (*Ber.*, 1906, **39**, 1722—1732).—The nitriles of α-amino-acids are formed when equal molecular quantities of potassium cyanide and ammonium chloride react in aqueous or aqueous-alcoholic solution with aldehydes or ketones of the aliphatic, aromatic, or hydroaromatic series (compare Ljubavin, Abstr., 1883, 178; Eschweiler, Abstr., 1894, i, 267; Curtius and Jay, *ibid.*, i, 162; Gulewitsch, Abstr., 1900, i, 476). The probable course of the reaction is indicated in the scheme: $KCN + H_2O \rightleftharpoons KOH + HCN$; $R{\cdot}CO{\cdot}R$(or H) + HCN = R(or H)$CR(OH){\cdot}CN$; $NH_4Cl + KOH = NH_3 + KCl + H_2O$; R(or H)$CR(OH){\cdot}CN + NH_3 = H_2O +$ R(or H)$CR(NH_2){\cdot}CN$.

The nitrile of α-aminophenylacetic acid was obtained from benzaldehyde in 60 per cent. yield, and α-amino*iso*butyric acid from acetone in 72·8 per cent. yield.

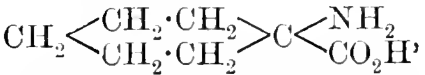
The following new compounds are described:

α-*Aminocyclohexylacetic acid*,  $CH_2{<}\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}{>}CH{\cdot}CH(NH_2){\cdot}CO_2H$, obtained from hexahydrobenzaldehyde in 80 per cent. yield, separates from water in crystalline nodules and melts and decomposes at 297°. The *picrate* crystallises in yellow prisms and melts and decomposes at 186—187°.

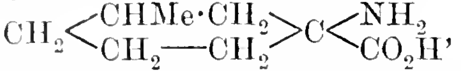
3-*Amino*-1-*methyl*cyclo*pentane*-3-*carboxylic acid*,



obtained from 1-methyl*cyclo*pentane-3-one in 59 per cent. yield, is very soluble in water, and melts and decomposes at 299—300°. In aqueous solution, the acid does not exhibit optical activity, although it is obtained from an active ketone (Abstr., 1902, i, 597). The *copper* salt forms blue anhydrous crystals.

1-*Amino*cyclo*hexane*-1-*carboxylic acid*,  $CH_2{<}\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}{>}C{<}\begin{matrix}NH_2\\CO_2H\end{matrix}$, obtained from *cyclo*hexanone in 93 per cent. yield, separates from water in octahedral crystals or in long prisms, and melts and decomposes at 334—335°. The *hydrochloride* softens at 280° and melts and decomposes at 310°. The *copper* salt forms dark blue crystals containing $1H_2O$. The *picrate* melts and decomposes at 209—210°.

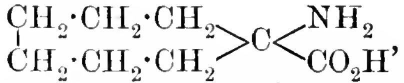
3-*Amino*-1-*methyl*cyclo*hexane*-3-*carboxylic acid*,



$$CH_2<\begin{matrix}CHMe\cdot CH_2\\ CH_2—CH_2\end{matrix}>C<\begin{matrix}NH_2\\ CO_2H\end{matrix},$$

obtained from 1-methyl*cyclo*hexane-3-one in 52 per cent. yield, separates from water in small plates containing $1H_2O$, and when anhydrous melts and decomposes at 330°. In acetic acid solution, it is optically inactive, although derived from an active ketone.

1-*Amino*cyclo*heptane*-1-*carboxylic acid*,



$$\begin{matrix}CH_2\cdot CH_2\cdot CH_2\\ | \\ CH_2\cdot CH_2\cdot CH_2\end{matrix}>C<\begin{matrix}NH_2\\ CO_2H\end{matrix},$$

obtained from suberone, separates from water in aggregates of glistening prisms containing 1 mol. H_2O. The anhydrous acid melts and decomposes at 306—307°, the *picrate* at 215—216°. The *copper* salt exists in three forms: bluish-violet plates containing 1 mol. H_2O, small, sky-blue anhydrous crystals, and reddish-violet needles. C. S.

Phenylation in the Presence of Copper as a Catalyst.

IRMA GOLDBERG (*Ber.*, 1906, **39**, 1691—1692).—A theoretical yield of phenylanthranilic acid may be obtained by interaction of anthranilic acid and bromobenzene in presence of a trace of copper. *p*-Bromonitrobenzene and anthranilic acid yield similarly 4-nitrophenylanthranilic acid.

The action may also be extended to acid amides. Benzamide reacts with bromobenzene in the presence of copper to form benzanilide Similarly, salicylanilide may be prepared from salicylamide.

A. McK.

Action of Ammonium Cyanide on Ketones of the Series $CO(C_nH_{2n-7})(C_nH_{2n+1})$.

J. JAWELOFF (*Ber.*, 1906, **39**, 1195—1200. Compare this vol., i, 409).—The action of ammonium cyanide on ketones of the series $CO(C_nH_{2n-7})(C_nH_{2n+1})$ leads to the formation of amino-nitriles and of amino-acids; the yields are diminished by the proximity of an aryl group to the carbonyl, and by the presence of *o*-methyl groups.

a-Amino-a-phenylpropionitrile hydrochloride is formed in a yield of 47 per cent., together with *a*-amino-*a*-phenylpropionic acid in a yield of 2 per cent. of the theoretical, by the action of ammonium cyanide on phenyl methyl ketone at 80° under pressure. The amino-nitrile hydrochloride, $CN\cdot CMePh\cdot NH_2,HCl$, forms small, yellow needles, melts at 96—97°, and is readily soluble in water or absolute alcohol, but is insoluble in ether, benzene, or carbon disulphide; the aqueous solution is acid to litmus, but does not change the colour of congo red. When slowly evaporated in absolute alcoholic solution, the aminonitrile hydrochloride yields ammonium chloride, and on recrystallisation from water it is decomposed, forming acetophenone. It is oxidised to benzoic acid by dilute alkaline permanganate solution, and on reduction with sodium and alcohol yields ammonia and *a*-phenylethylamine. *a-Amino-a-phenylpropionitrile* is a dark oil, which boils and partially decomposes at 101—104° under 12·5 mm. pressure. *α-Amino-α-phenylpropionamide hydrochloride*, $NH_2 \cdot CO \cdot CMePh \cdot NH_2,HCl$, crystallises in large, colourless prisms, melts above 250°, and is readily soluble in water.

α-Amino-α-p-tolylpropionitrile hydrochloride,

$CN \cdot CMe(C_7H_7) \cdot NH_2,HCl$,

is formed from *p*-tolyl methyl ketone in a yield of 42 per cent. of the theoretical; it crystallises in small, slightly yellow needles and melts at 104—105°. *α-Amino-α-p-tolylpropionic acid*, $NH_2 \cdot CMe(C_7H_7) \cdot CO_2H$, formed together with the amino-nitrile, crystallises from water in sheaves of long, white, silky needles, sublimes but does not melt, and forms an insoluble *copper* salt.

α-Amino-α-3 : 4-xylylpropionitrile hydrochloride,

$CN \cdot CMe(C_6H_3Me_2) \cdot NH_2,HCl$,

which crystallises in yellow needles and melts at 103—104°, and *α-amino-α-3 : 4-xylylpropionic acid*, $NH_2 \cdot CMe(C_6H_3Me_2) \cdot CO_2H$, crystallising in long, white needles, are formed together from 3 : 4-xylyl methyl ketone in yields of 38 per cent. and 11 per cent. of the theoretical respectively.

α-Amino-α-2 : 4-xylylpropionitrile hydrochloride, $C_{11}H_{14}N_2,HCl$, which crystallises in yellow needles and melts at 97—98°, and the corresponding *amino-acid*, $C_{11}H_{15}O_2N$, crystallising in small plates, are formed together from 2 : 4-xylyl methyl ketone in yields of 13 per cent. and 8 per cent. of the theoretical respectively.

α-Amino-α-2 : 5-xylylpropionitrile hydrochloride, melting at 101—102°, and the corresponding *amino-acid*, crystallising in small plates, are formed from 2 : 5-xylyl methyl ketone in yields of 12 per cent. and 8 per cent. of the theoretical respectively.

α-Amino-α-phenylbutyronitrile hydrochloride, $CN \cdot CEtPh \cdot NH_2,HCl$, is obtained from phenyl ethyl ketone in a yield of 42 per cent. of the theoretical; it crystallises from water or alcohol in small, yellow needles and melts at 118—119°. The corresponding *amino-acid*, which is obtained in a yield of 5 per cent. of the theoretical, crystallises in small, colourless prisms.

The interaction of benzylacetone and ammonium cyanide leads to the formation of *α-amino-β-benzyl*iso*butyronitrile hydrochloride*, $CH_2Ph \cdot CH_2 \cdot CMe(CN) \cdot NH_2,HCl$, which is obtained in a yield of 66 per cent., together with *α-amino-β-benzyl*iso*butyric acid*, which is obtained in a yield of 6 per cent. of the theoretical and crystallises in short, white needles. The amino-nitrile hydrochloride crystallises in colourless, greasy prisms, or from alcohol or water in colourless plates, and melts and decomposes at 120—122·5°. G. Y.

Reaction between Unsaturated Compounds and Organic Magnesium Compounds. VIII. Reactions with αβ-Unsaturated Nitriles. Elmer P. Kohler (*Amer. Chem. J.*, 1906, **35**, 386—404. Compare Abstr., this vol., i, 96, and previous abstracts).—When α-phenylcinnamonitrile is added gradually to a boiling solution of magnesium ethyl bromide and the resulting magnesium compound is treated with ice-water and hydrochloric acid, two racemic modifications of *αβ-diphenylvaleronitrile*, $CHPhEt \cdot CHPh \cdot CN$, are produced, one of which forms small, lustrous crystals, melts at 115°, and is readily soluble in acetone or boiling alcohol, and moderately so in ether, whilst the other is obtained as a colourless oil. On hydrolysing these nitriles by heating them with strong hydrochloric acid at 180° for four hours, a mixture of *αβ-diphenylvaleric acids*, $CHPhEt\cdot CHPh\cdot CO_2H$, is produced in each case. One of these acids crystallises in small, lustrous plates, melts at 178°, and is moderately soluble in ether, and slightly so in light petroleum; the other acid forms clusters of crystals, melts at 152—153°, and is readily soluble in alcohol or ether, and sparingly so in light petroleum. Each of these acids, when heated with concentrated hydrochloric acid at 180° for twenty-four hours, yields a mixture of the two forms.

αβ-Diphenyl-α-ethylvaleronitrile, $CHPhEt\cdot CPhEt\cdot CN$, obtained by the action of ethyl iodide on the magnesium derivative, crystallises in large, tabular plates, melts at 105°, and is readily soluble in acetone, alcohol, ether, or chloroform. Attempts to hydrolyse this substance were unsuccessful. On reduction with sodium and boiling amyl alcohol, *γδ-diphenylhexane* is produced which melts at 92°, boils at 175° under 20 mm. pressure, and is readily soluble in organic solvents.

αβ-Diphenyl-α-methylvaleronitrile crystallises in prisms, melts at 99°, is readily soluble in alcohol or ether, and cannot be hydrolysed.

αβ-Diphenyl-α-benzylvaleronitrile, $CHPhEt\cdot CPh(C_7H_7)\cdot CN$, crystallises from benzene in needles containing 1 mol. of the solvent, which it loses slowly at the ordinary temperature; it melts at 140°, and is readily soluble in benzene, acetone, or hot alcohol.

Although all these alkyl derivatives should be capable of existing in two inactive modifications, only one substance was obtained in each case. It is evident, therefore, that only one magnesium compound is formed by the union of phenylcinnamonitrile with magnesium ethyl bromide, and that the two stereoisomeric diphenylvaleronitriles are produced by the decomposition of this substance with water.

α-Benzoyl-αβ-diphenylvaleronitrile, $CHPhEt\cdot CPhBz\cdot CN$ or

$$CHPhEt\cdot CPh\colon C\colon NBz,$$

obtained by the action of benzoyl chloride on the magnesium derivative, crystallises from alcohol in large needles, melts at 137°, is readily soluble in chloroform, acetone, or hot alcohol, moderately so in cold alcohol or ether, and is easily hydrolysed with formation of benzoic acid and the solid diphenylvaleronitrile.

α-Cyano-αβ-diphenylvaleric acid, $CHPhEt\cdot CPh(CN)\cdot CO_2H$ or

$$CHPhEt\cdot CPh\colon C\colon N\cdot CO_2H,$$

obtained by the decomposition of the product of the action of carbon dioxide on the magnesium derivative, is an oil which is fairly stable at low temperatures, but slowly evolves carbon dioxide at the ordinary temperature, and is instantly decomposed by boiling water; the salts are less stable than the acid itself.

Both modifications of diphenylvaleronitrile react with magnesium methyl iodide with the formation, in each case, of two stereoisomeric forms of *γδ-diphenylhexane-β-one*, $CHPhEt\cdot CHPh\cdot COMe$. One of these forms crystallises in stout needles, melts at 116°, and is readily soluble in ether or acetone, and moderately so in cold alcohol. The other form crystallises from light petroleum and melts at 56°.

By the action of magnesium phenyl bromide on the two modifications of diphenylvaleronitrile, two forms of *αβ-diphenylvalerophenone*, CHPhEt·CHPh·COPh, are obtained, one of which crystallises in needles, melts at 170°, and dissolves readily in acetone or chloroform; the other form crystallises in plates, melts at 92°, and is easily soluble in alcohol or ether.

Magnesium phenyl bromide reacts with phenylcinnamonitrile with formation of triphenylpropionitrile and benzylidenedeoxybenzoin. *Triphenylpropionitrile*, $CHPh_2$·CHPh·CN, crystallises in plates, melts at 102°, and is readily soluble in alcohol or ether. *Triphenylpropionamide*, $CHPh_2$·CHPh·CO·NH_2, obtained by heating the nitrile at 160° for four hours with concentrated hydrochloric acid, crystallises in needles, melts at 213°, is readily soluble in alcohol, moderately so in ether, and slightly so in boiling water; it is easily hydrolysed by strong hydrochloric acid at 200° with formation of triphenylpropionic acid. *Triphenylethylpropionitrile*, $CHPh_2$·CPhEt·CN, obtained together with benzylidenedeoxybenzoin by the action of ethyl iodide on a solution of the magnesium derivative, crystallises in needles, melts at 134°, dissolves readily in alcohol or ether, and undergoes no change when heated to 200° with concentrated hydrochloric acid.

By the interaction of cinnamonitrile with magnesium methyl iodide and with magnesium phenyl bromide, products are obtained which yield dibenzylideneacetone and benzylideneacetophenone respectively. β-Phenylcinnamonitrile reacts similarly with magnesium phenyl bromide with production of β-phenylbenzylideneacetophenone.

E. G.

Stereoisomeric Cinnamic Acids. Emil Erlenmeyer, jun., and C. Barkow (*Ber.*, 1906, **39**, 1570—1585. Compare Erlenmeyer, jun., Abstr., 1905, i, 892).—The brucine salt melting at 135° is formed by the action of brucine on cinnamic acid from storax in absolute alcoholic solution; it crystallises in monoclinic plates [$a:b:c = 1\cdot2039:1:0\cdot7770$; $\beta = 77°39'$], dissolves in 16·44 parts of 50 per cent. ether-alcohol, and has $[\alpha]_D$ −5° in a 0·5 per cent., $[\alpha]_D$ ±0° in a 1 per cent., or $[\alpha]_D$ +12·5° in a 10 per cent. solution in absolute alcohol. The brucine salt melting at 113° is formed by the action of brucine on cinnamic acid from storax in 50 per cent. alcoholic solution; it crystallises in monoclinic plates [$a:b:c = 2\cdot3026:1:1\cdot4989$; $\beta = 80°45'$], and when dried loses C_2H_6O and commences to melt at 113°. It dissolves in 8·23 parts of 50 per cent. ether-alcohol, and has, when dried, $[\alpha]_D$ −16·67° in a 1 per cent., or, when containing C_2H_6O, $[\alpha]_D$ −12·5° in a 1 per cent., or $[\alpha]_D$ +3·33° in a 10 per cent. solution in absolute alcohol. In one experiment, when heated with alcohol, this salt was converted into that melting at 135°.

The brucine salt melting at 107° is the racemic compound of the salts melting at 135° and 113°, into which it is resolved by recrystallisation from a mixture of alcohol and ether; it dissolves in 6·92 parts of 50 per cent. ether-alcohol, and has $[\alpha]_D$ −16·7° in a 0·5 per cent. or $[\alpha]_D$ ±0° in a 5 per cent. solution in absolute alcohol.

α-Cinnamic acid obtained from the brucine salt melting at 135° is identical with the acid from storax; it crystallises in monoclinic plates

[$a:b:c=0\cdot8618:1:0\cdot3142$; $\beta=82°52'$], melts at 134—135°, dissolves in 19·8 parts of 75 per cent. alcohol, and is converted into β-cinnamic acid when heated above its melting point, or dissolved in a small quantity of ether and precipitated by addition of light petroleum, or recrystallised from 75 per cent. alcohol.

β-Cinnamic acid is obtained from Honduras balsam or from the brucine salt melting at 113°; it crystallises in monoclinic plates [$a:b:c=3\cdot8855:1:3\cdot0240$; $\beta=89°12'$], melts at 133°, dissolves in 13·12 parts of 75 per cent. alcohol, and is converted into the α-acid by repeated recrystallisation from ether, or on recrystallisation from absolute alcohol.

The acid obtained from the brucine salt melting at 107° crystallises from ether in large, thin leaflets, dissolves in 18·02 parts of 75 per cent. alcohol, and when freshly prepared can be reconverted into the brucine salt melting at 107°.

Synthetical cinnamic acid dissolves in 15·97 parts of 75 per cent. alcohol; it yields β-cinnamic acid under the same conditions as does the acid from storax, but in smaller crystals. If the synthetical acid is dissolved in hot 75 per cent. alcohol and cooled, β-cinnamic acid crystallises out together with a small amount of the α-acid, into which it changes entirely if left in contact with the solution. But if the β-acid is filtered off, the mother liquor evaporated to dryness, and the residue again recrystallised from 75 per cent. alcohol, a further amount of β-acid is obtained, which changes into the α-acid only extremely slowly.

Whilst in absolute alcoholic solution α-cinnamic acid forms the brucine salt melting at 135° quantitatively, the synthetical acid yields only half of the theoretical amount of this salt, but in 50 per cent. alcoholic solution it forms the salt melting at 113° quantitatively.

The acid obtained from storax after treatment with boiling sodium hydroxide dissolves in 15·01 parts of 75 per cent. alcohol.

Six cinnamic acids differing in crystallographical as also in other properties are now known: Erlenmeyer, sen.'s, *iso*cinnamic acid, melting at 37—38°; *allo*cinnamic acid, melting at 68°; Liebermann's *iso*cinnamic acid, melting at 59°; triclinic cinnamic acid, melting at 80°; α-cinnamic acid from storax, melting at 134—135°; and β-cinnamic acid from storax, melting at 132—133°. To these must be added *iso*cinnamic acid from the most soluble brucine salt, which differs from Liebermann's acid only slightly in its crystalline form, and the synthetical acid, which differs from the storax acid in its manner of crystallisation and in the formation of the brucine salt. G. Y.

Preparation of Glycidic Esters and Aldehydes in the Hexahydroaromatic Series. Georges Darzens and P. Lefébure (*Compt. rend.*, 1906, 142, 714—715. Compare Abstr., 1905, i, 116; this vol., i, 62, 137).—*cyclo*Hexanone and its three methyl homologues (Sabatier and Senderens, Abstr., 1904, i, 156; 1905, i, 275) condense with ethyl chloroacetate to form $\beta\beta$-substituted glycidic esters, which on distillation yield the corresponding hexahydrobenzaldehyde. The *compound*

$C_6H_{10}<\overset{O}{\underset{CH\cdot CO_2Et}{|}}$ is a viscous, colourless liquid which boils at 128—129° under 17 mm. pressure, has an extremely disagreeable odour of rotten fruits and of scatole, and yields hexahydrobenzaldehyde (compare Bouveault, Abstr., 1904, i, 61; 1905, i, 116) on distillation under a pressure of 30 mm. The *compounds* obtained by condensing ethyl chloroacetate and *o*-, *m*-, or *p*-methyl*cyclo*hexanone boil at 129—131° under 15 mm. pressure, 140—143° under 20 mm. pressure, or 133° under 18 mm. pressure respectively; they are all characterised by their extremely disagreeable odour, and yield the corresponding methylhexahydrobenzaldehyde on distillation; *hexahydro-*o*-tolualdehyde* boils at 61—62° under 15 mm. pressure, has a strong odour of camphor, and forms a semicarbazone which melts at 137—138°; hexahydro-*m*-tolualdehyde (compare Tschitschibabin, Abstr., 1904, i, 421) boils at 60—61° under 15 mm. pressure, and *hexahydro-*p*-tolualdehyde* is a liquid with a characteristic aromatic odour, which boils at 64—65° under 16 mm. pressure and forms a semicarbazone which melts at 168—169°. M. A. W.

Substitution of the Acetyl by the Methyl Group by means of Diazomethane. JOSEF HERZIG and J. TICHATSCHEK (*Ber.*, 1906, **39**, 1557—1559. Compare this vol., i, 173).—Acetanilide and phenacetin do not react with diazomethane. On treatment with diazomethane and hydrolysis of the product with potassium hydroxide, *p*-acetoxybenzoic and *m*-acetoxybenzoic acids yield acids containing 73·4 per cent. and 88·6 per cent. of the corresponding methoxybenzoic acids respectively, whilst *p*-hydroxybenzoic acid yields pure anisic acid. Under similar conditions, salol forms the methyl ether quantitatively, but salicylic acid yields a product containing only 1·27 per cent. of the methyl ether, and the acetyl groups of acetylsalicylic acid and acetylsalol remain unchanged. G. Y.

Synthesis of α-Amino-acids. FRANZ KNOOP and HANS HOESSLI (*Ber.*, 1906, **39**, 1477—1480. Compare Knoop, Abstr., 1905, ii, 46). —Fittig and Petkow's α-keto-γ-phenylbutyric acid (Abstr., 1898, i, 196) yields an *oxime*, $CH_2Ph{\cdot}CH_2{\cdot}C(NOH){\cdot}CO_2H$, which crystallises in colourless needles, melts at 165°, and dissolves readily in most organic solvents with the exception of light petroleum. *α-Amino-γ-phenylbutyric acid*, $CH_2Ph{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H$, is obtained when the oxime is reduced with sodium amalgam and water, care being taken to neutralise the free alkali from time to time with hydrochloric acid. It crystallises from water in colourless plates or needles, and melts and decomposes at 293—295° when quickly heated. It is tasteless, dissolves sparingly in cold water, and is insoluble in all organic solvents with the exception of ethyl alcohol. The aqueous solution does not dissolve cupric oxide or carbonate. Better yields are obtained when the reduction is accomplished by means of aluminium amalgam and moist ether. The same method of reduction is used with advantage in the preparation of phenylalanine.

The constitution of α-keto-γ-phenylbutyric acid has been confirmed by its quantitative oxidation to β-phenylpropionic acid by means of hydrogen peroxide. Hence the amino-acid described by Fischer and

Schmitz (this vol., i, 182) under the same name must have a different constitution. J. J. S.

Condensation of Acetylenic Amides with Phenols. General Method of Synthesis of β-Substituted Derivatives of β-Phenoxyacrylamides. Charles Moureu and I. Lazennec (*Compt. rend.*, 1906, **142**, 894—895. Compare this vol., ii, 240, 276).—The β-substituted β-phenoxyacrylamides are obtained by heating at 130—140° the sodium derivative of phenol with the acetylenic amide dissolved in phenol. *β-o-Tolyloxy-β-amylacrylamide*,

$C_5H_{11}\cdot C(O\cdot C_6H_4Me)\colon CH\cdot CO\cdot NH_2$,

and *β-phenoxy-β-hexylacrylamide*, $C_6H_{13}\cdot C(OPh)\colon CH\cdot CO\cdot NH_2$, are oily substances. *β-Phenoxy-β-phenylacrylamide*, $OPh\cdot CPh\colon CH\cdot CO\cdot NH_2$, melts at 195—197°, *β-o-tolyloxy-β-phenylacrylamide*,

$C_6H_4Me\cdot O\cdot CPh\colon CH\cdot CO\cdot NH_2$,

at 168°, and *β-guaiacoxy-β-phenylacrylamide*,

$OMe\cdot C_6H_4\cdot O\cdot CPh\colon CH\cdot CO\cdot NH_2$,

at 158°. When heated with dilute sulphuric acid, these substituted acrylamides are hydrolysed with the formation of the corresponding ketone and phenol; thus, β-phenoxy-β-hexylacrylamide yields methyl hexyl ketone and phenol. H. M. D.

Fermentation Vats. Hermann Wendelstadt and Arthur Binz (*Ber.*, 1906, **39**, 1627—1631).—Woad fermentations may be conducted on the small scale in glass vessels provided atmospheric oxygen is not allowed to enter. Experiments are most readily conducted in a litre flask provided with a cork and a delivery tube the end of which dips under water. Attempts have been made to isolate the characteristic organism which causes the fermentation. The addition of disinfectants, or sterilisation by heating, renders woad non-fermentable. J. J. S.

Linking Up of Amino-acids. Hans Meyer (*Ber.*, 1906, **39**, 1451—1452).—A considerable amount of anthranilo-anthranilic acid (Anschütz, Schmidt, and Greiffenberg, Abstr., 1903, i, 57; Mohr and Köhler, D.R.-P. 127138) is obtained as a by-product in the preparation of anthranilic acid according to D.R.-P. 55988. J. J. S.

Tautomerism of *cyclo*Hexanone. Carl Mannich (*Ber.*, 1906, **39**, 1594—1595).—When boiled with acetic anhydride and sodium acetate in a reflux apparatus, *cyclo*hexanone forms *tetrahydrophenyl acetate*, $C_6H_9\cdot O\cdot Ac$, which is obtained as a colourless oil with a pleasant fruity odour. The acetate boils at 180—182°, is hydrolysed completely by boiling alcoholic potassium hydroxide, and when treated with semicarbazide hydrochloride and potassium hydroxide in dilute alcoholic solution yields the semicarbazone of *cyclo*hexanone. In slightly alkaline solution, the acetate is oxidised by potassium permanganate, forming adipic acid. G. Y.

Ketones obtained by means of *n*-Valeric Acid. E. Layraud (*Bull. Soc. chim.*, 1906, [iii], **35**, 223—235).—Phenyl butyl ketone, obtained by condensing valeryl chloride with benzene in presence of aluminium chloride, boils at 248·5° (corr.) and has n_D 1·5152 at 19° (compare Perkin and Calman, Trans., 1886, **49**, 161). The *oxime* separates from ether in colourless, silky needles, melts at 52—52·5°, is readily soluble in alcohol or benzene, less so in light petroleum, and is converted by phosphorus pentachloride into a mixture of benzoylbutylamine and valerylaniline. The *semicarbazone* crystallises from boiling alcohol in silky needles and melts at 166°.

p-Tolyl butyl ketone, similarly prepared, crystallises in bulky monoclinic prisms. The *oxime* is a viscous, colourless liquid and boils at 180° under 25 mm. or at 168° under 13 mm. pressure, and undergoes the Beckmann transformation with phosphorus pentachloride. The semicarbazone melts at 206° (compare Blaise, Abstr., 1902, i, 164).

p-*Xylyl butyl ketone* ($Me_2 : CO = 1 : 4 : 6$), similarly prepared from *p*-xylene and valeryl chloride, is a colourless liquid of pleasant odour, boils at 266·5° under 762 mm. pressure, and is miscible with organic solvents. The *oxime* is oily and distils at 175—176° under 19 mm. pressure. The *semicarbazone* is crystalline, melts at 139°, and is less soluble in alcohol than its lower homologue.

m-*Xylyl butyl ketone* ($Me_2 : CO = 1 : 3 : 6$) is a slightly oily, colourless liquid and boils at 149° under 16 mm. pressure. On oxidation with chromic acid, dissolved in acetic acid, it yields 2 : 4-dimethylbenzoic acid. The *oxime* is a viscous, yellow liquid and distils at 184—187° under 21 mm. pressure. The *semicarbazone* crystallises from boiling alcohol and melts at 188°.

p-*Phenylethyl butyl ketone* is a colourless liquid and boils at 163—164° under 27 mm. pressure, or at 173—174° under 33 mm. pressure. On oxidation with chromic acid dissolved in acetic acid, it yields *p*-ethylbenzoic acid. The *oxime* is a viscous liquid and boils at 193—194° under 21 mm. pressure. The *semicarbazone* crystallises from boiling methyl alcohol and melts at 190·5°.

p-*Anisyl butyl ketone* crystallises in large prisms, melts at 27—28°, boils at 196·5° under 40 mm. pressure, and is readily soluble in alcohol and ether. On oxidation with chromic acid, it yields butyric and anisic acids. The *semicarbazone* crystallises from boiling alcohol, melts at 164°, and is slightly soluble in benzene or ether.

p-*Phenetyl butyl ketone* crystallises in colourless needles, melts at 31°, is almost inodorous, and on oxidation with chromic acid yields *p*-ethoxybenzoic acid. The *semicarbazone* crystallises in needles, melts at 192°, and is slightly soluble in light petroleum or benzene, more so in ether or chloroform. T. A. H.

Behaviour of Ammonium Cyanide with Ketones of the Series $CO(C_nH_{2n-7})_2$. W. Wiekmann (*Ber.*, 1906, **39**, 1200. Compare this vol., i, 409, 426).—Ammonium cyanide does not interact with benzophenone or phenyl *p*-tolyl ketone in alcoholic solution at 80° under pressure. G. Y.

Nitro-derivatives of Tetramethyldiaminobenzophenone. Alfred Kliegl (*Ber.*, 1906, **39**, 1266—1275. Compare Nathanson and Müller, Abstr., 1889, 1188; Grimaux, Abstr., 1898, i, 581).—The nitration of Michler's ketone is most readily effected by adding a mixture of 66 per cent. nitric acid and concentrated sulphuric acid to a well-cooled solution of the ketone in concentrated sulphuric acid.

When the mono-nitro-derivative is reduced with stannous chloride and hydrochloric acid between −5° and +5°, it gives a 50 per cent. yield of 3-*amino*-4 : 4′-*tetramethyldiaminodiphenyl ketone*,

$$NH_2\cdot C_6H_3(NMe_2)\cdot CO\cdot C_6H_4\cdot NMe_2,$$

which crystallises in dark yellow prisms melting at 138·75—139° and dissolves only sparingly in ether. The *oxime*, $C_{17}H_{22}ON_4$, crystallises in intensely yellow needles, sinters at 192°, and melts at 194·5—196·5°. It dissolves sparingly in ether, benzene, or carbon tetrachloride. The *acetyl* derivative, $C_{19}H_{23}O_2N_3$, melts at 153·5—154·5°, crystallises from 70 per cent. alcohol and is only sparingly soluble in ether or light petroleum. The *benzoyl* derivative, $C_{24}H_{25}O_2N_3$, melts at 190·5—192·5°.

3-*Acetylamino*-4 : 4′-*tetramethyldiaminobenzhydrol*, $C_{19}H_{25}O_2N_3$, is obtained when the acetyl derivative of the ketone is reduced in the cold with zinc dust and 10—20 per cent. hydrochloric acid, and the filtered solution poured into sodium hydroxide solution at 0°. It crystallises from a mixture of acetone and water in thick, colourless prisms melting at 145·5—146°, is only sparingly soluble in ether or light petroleum, and gives a blue coloration when warmed with glacial acetic acid. The corresponding *benzoyl* derivative, $C_{24}H_{27}O_2N_3$, melts at 180·5—181·5°.

3 : 3′-*Diamino*-4 : 4′-*tetramethyldiaminodiphenyl ketone*, obtained by the reduction of the corresponding dinitro-compound with stannous chloride and hydrochloric acid in alcoholic solution at low temperatures, crystallises from alcohol or ethyl acetate in glistening, golden-yellow plates and melts at 145—145·5°. The *oxime* crystallises from benzene in slender, colourless needles having the composition $C_{17}H_{23}ON_5,C_6H_6$. After loss of the benzene, it melts at 168°, and is readily decomposed by hydrochloric acid. The *benzoyl* derivative, $C_{31}H_{30}O_3N_4$, crystallises from glacial acetic acid in pale yellow plates melting at about 199·5—201°.

2-Acetylamino-4 : 4′-tetramethyldiaminodiphenylmethane (D.R.-P. 79250), obtained by acetylating Ullmann and Maric's 2-amino-4 : 4′-tetramethyldiaminodiphenylmethane (Abstr., 1902, i, 182), melts at 138°, and when oxidised with an alcoholic solution of chloranil yields 2-*acetylamino*-4 : 4′-*tetramethyldiaminodiphenyl ketone*, $C_{19}H_{23}O_2N_3$, which crystallises in lemon-yellow prisms melting at 162·25° and sparingly soluble in ether. When hydrolysed, it yields 2-*amino*-4 : 4′-*tetramethyldiaminobenzophenone*, melting at 205·5°, and quite distinct from the amino-compound obtained by reducing the mono-nitro-derivative of Michler's ketone, and hence the nitro-group in this latter occupies the position 3. 2-Acetylamino-4 : 4′-tetramethyldiaminobenzhydrol melts between 165° and 169°. J. J. S.

Action of Imino-esters and of Imino-chlorides on Organo-magnesium Derivatives. Raymond Marquis (*Compt. rend.*, 1906, 142, 711—713).—In addition to the methods already described by Blaise (Abstr., 1901, i, 133; 1902, i, 164) and by Béis (Abstr., 1904, i, 15) for the synthesis of ketones by means of organo-magnesium derivatives, the author finds that when methyl phenyliminobenzoate is heated at

100° with magnesium phenyl bromide in toluene solution, and the product decomposed by acid, benzophenoneanil is obtained, according to the equation $OMe\cdot CPh:NPh + MgBrPh = MgBr\cdot OMe + CPh_2:NPh$, and this is readily converted into benzophenone on boiling with dilute acids, the yield being 55 per cent. of the theoretical. Attempts to extend the method to the preparation of mixed ketones were unsuccessful generally. Ethyl phenyliminobenzoate and magnesium benzyl chloride, however, interact to form deoxybenzoin (phenyl benzyl ketone) with a yield of 10 per cent. of the theoretical, whilst the yield is increased to 60 per cent. if benzoylphenyliminochloride replaces the ethyl phenyliminobenzoate in the above reaction. M. A. W.

Condensation Products of Gallacetophenone. HANS RUPE and L. VEIT (*Zeit. Farb. Ind.*, 1906, **5**, 101—105).—o-*Nitrobenzylidenegallacetophenone*, $C_6H_2(OH)_3\cdot CO\cdot CH:CH\cdot C_6H_4\cdot NO_2$, prepared by condensing gallacetophenone with *o*-nitrobenzaldehyde by means of hydrogen chloride in alcoholic solution, crystallises from alcohol in long, lustrous, yellowish-green needles and melts at 212°. The *triacetyl* derivative, $C_{21}H_{17}O_9N$, crystallises from alcohol in small, yellow needles and decomposes at 165°.

On condensing triacetylgallacetophenone with *m*-nitrobenzaldehyde in presence of hydrogen chloride, m-*nitrobenzylidenegallacetophenone*, $C_{15}H_{11}O_6N$, or m-*nitrobenzylidenedigallacetophenone*,

$$NO_2\cdot C_6H_4\cdot CH[CH_2\cdot CO\cdot C_6H_2(OH)_3]_2,$$

is obtained, the product depending on the conditions; the acetyl groups are eliminated during the condensation. *m*-Nitrobenzylidenegallacetophenone crystallises from alcohol in small needles, melts at 94°, and gives a *triacetyl* derivative, $C_{21}H_{17}O_9N$, which crystallises from glacial acetic acid in silver-white needles and melts at 152°. m-*Nitrobenzylidenedigallacetophenone* crystallises from alcohol on adding water in yellow needles, melts and decomposes at 220—230°, and gives a *hexa-acetyl* derivative, $C_{35}H_{31}O_{16}N$, which forms silver-white needles and melts at 193°.

p-Nitrobenzaldehyde also gives two derivatives with gallacetophenone. p-*Nitrobenzylidenegallacetophenone* crystallises from alcohol on adding water in golden-yellow needles, melts at 138°, and gives a *triacetyl* derivative which crystallises from alcohol in slender, silky needles and melts at 158°. p-*Nitrobenzylidenedigallacetophenone* crystallises from dilute alcohol in feebly yellow needles and melts and decomposes at 212°; the *hexa-acetyl* derivative, $C_{35}H_{31}O_{16}N$, crystallises from alcohol in white needles and melts and decomposes at 185°.

Attempts to condense protocatechualdehyde with triacetylgallacetophenone in presence of hydrogen chloride gave only resinous products; experiments made with the dibenzoyl derivative of protocatechualdehyde were equally unsuccessful.

3 : 4-*Dihydroxybenzylidenegallacetophenone methylene ether*,

$$C_6H_2(OH)_3\cdot CO\cdot CH:CH\cdot C_6H_4<\substack{O\\O}>CH_2,$$

prepared by condensing triacetylgallacetophenone with piperonal by means of hydrogen chloride, crystallises from benzene in long, golden-yellow needles, melts at 208°, and gives a *triacetyl* derivative, $C_{22}H_{18}O_6$, which crystallises from alcohol in yellow needles and melts at 142°.

The comparative tinctorial value of the substances enumerated above is dealt with. W. A. D.

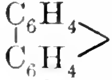
The Varying Values of Single Bonds. ALFRED WERNER (*Ber.*, 1906, 39. 1278—1292).—It is well known that different groups of unsaturated compounds appear to be unsaturated to different degrees. The three groups of diphenylethylene, ordinary ethylene, and fulgene compounds are compared. The members of the first group cannot combine with bromine, those of the second combine readily, and those of the third can even abstract oxygen from the atmosphere.

It is suggested that when the atom M in the compound $M\cdot X$ is linked with other atoms, its affinity may be so lessened that the greater part of the saturation capacity of X is not utilised, and thus is available for the formation of molecular compounds with other substances. As examples are cited the numerous cases of the formation of additive compounds between metallic haloids and compounds such as $SnCl_4$, PCl_5, PBr_5, WOCl, $POCl_3$, $SeOCl_2$, NO_2Cl, &c. Organic compounds of the type $CPh_3Cl,AlCl_3$, $CPh_3Cl,SnCl_4$, $2(CPh_3Cl,3HgCl_2)$, $CPh_3Cl,ZnCl_2$, and similar derivatives are also quoted. Experiments have proved that when the phenyl groups in the triphenylchloromethane are replaced by other negative groups, such as benzoyl, the products are not always so reactive as the triphenylmethane derivatives. Benzoyldiphenylbromomethane reacts with alcohols in the same manner as triphenylchloromethane, as does also benzoyldiphenylene bromomethane, but tribenzoylmethane may be boiled for hours with alcohols without decomposition. The reactivity of the haloid derivatives of triphenylmethane and their formation of additive compounds is attributed to the small saturation value of the CPh_3 group, and it is argued that in $CHPh_3$ there should be a considerable residual affinity of the H atom, and the compound should therefore yield additive derivatives. Several of these are cited.

[With PH. GERHARDT.]—*Benzoyldiphenylbromomethane*,

$$CPh_2Br\cdot COPh,$$

obtained by brominating triphenylvinyl alcohol in chloroform solution, crystallises from a mixture of ether and light petroleum in colourless needles melting at 99°, and dissolves readily in most organic solvents. When boiled with methyl alcohol, it yields the *methyl ether* of benzoyldiphenylcarbinol, $OMe\cdot CPh_2\cdot COPh$, which crystallises in colourless plates melting at 94°. The corresponding *ethyl ether* melts at 85°. When boiled with aqueous acetone, the bromo-derivative yields phenylbenzoin.

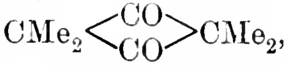
[With G. SCHÖLER.]—*Benzoylfluorene*, $C_{20}H_{14}O$, obtained by the Claisen reaction from ethyl benzoate and fluorene, crystallises from methyl alcohol in long needles melting at 138°. *Benzoyldiphenylenebromomethane*,  $\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!\!>CBr\cdot COPh$, obtained by the action of bromine on a benzene solution of benzoylfluorene, forms small, monoclinic crystals melting at 145°. The *methyl ether*,  $\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!>C(OMe)\cdot COPh$, separates from its solution in light petroleum as small, rhombic crystals.

[With W. ZIPSER.]—*Tribenzoylbromomethane*, $CBr(COPh)_3$, obtained by brominating a chloroform solution of tribenzoylmethane, crystallises from ether in glistening needles and melts at 89°.

[With A. SUMMERER.]—Triphenylmethane forms an *additive* product with aniline, $CHPh_3,NH_2Ph$, in the form of colourless, cubical crystals melting at 84°. The *o*-toluidine additive *compound* forms large, transparent, rhombic plates.

m-Nitrophenylnaphthaxanthen (Zenoni, Abstr., 1894, i, 136) forms an additive compound, $C_{33}H_{23}O_3N$, with benzene in the form of yellow, glistening crystals.

Ethyl tetranitrodiphenylacetate (Richter, *Ber.*, 1888, **21**, 2471) is best prepared by nitrating ethyl diphenylacetate. It yields an *additive* compound, $C_{22}H_{19}O_{10}N_5$, with aniline, which separates from alcohol as a voluminous, golden-yellow precipitate. When exposed to the air or heated at 91°, it turns black and melts and decomposes at 96·5°. The *additive* compound with naphthalene, $C_{42}H_{32}O_{20}N_8$, crystallises in colourless needles melting at 156°. J. J. S.

Synthesis of a Ketone of the *cyclo*Butane Series. EDGAR WEDEKIND and W. WEISSWANGE (*Ber.*, 1906, **39**, 1631—1646).—1 : 3-*Diketotetramethyl*cyclo*butane*,  $CMe_2\!<\!\begin{matrix}CO\\ CO\end{matrix}\!>\!CMe_2$, is obtained when a solution of *iso*butyryl chloride in dry carbon disulphide is dropped into a solution of triethylamine in the same solvent, great care being taken that all the substances are dry and that atmospheric moisture is excluded. After removal of trimethylamine hydrochloride, an oil is obtained from which crystals of the ketone gradually separate; they are most readily purified by washing with light petroleum and then subliming. The yield is under 20 per cent. The ketone has an odour resembling that of menthol or camphor, is extremely volatile, and passes over with ether vapour. It crystallises well, melts at 115—116°, has n_D 1·4991 at 15° and a sp. gr. 0·8875, dissolves readily in most organic solvents with the exception of light petroleum, but is only sparingly soluble in water. It gives no coloration with ferric chloride and does not decolorise bromine or permanganate. With ammonia at 120—130°, it yields a product melting at 108°. The *dioxime*, $C_8H_4O_2N_2$, crystallises from alcohol in colourless plates melting at 281° and is insoluble in water or ether. The *bisphenylhydrazone*, $C_{20}H_{24}N_4$, forms colourless plates melting at 207—208°, and does not give Pechmann's osazone reaction. The *disemicarbazone*, $C_{10}H_{18}O_2N_6$, begins to sinter at 282° and melts and decomposes at 298°. The ketone condenses with *o*-phenylenediamine yielding a *product*, $C_{14}H_{18}ON_2$, which crystallises from boiling ethyl acetate in glistening plates melting at 248—249°. It yields an *acetyl* derivative melting at 150—151° and does not give the ordinary quinoxaline reactions.

[With L. ERDMANN.]—Tetramethyldiketo*cyclo*butane can also be obtained by the action of the copper-zinc couple on a dry ethereal solution of *α*-bromo*iso*butyryl bromide. The condensation product with phenylcarbimide, $C_{11}H_{11}O_2N$, melts at 239°. J. J. S.

1-Methyl*cyclo*pentane-2 : 4 : 5-trione. I. Otto Diels, Johannes Sielisch, and Ernst Müller (*Ber.*, 1906, **39**, 1328—1340).—Since acetone condenses with ethyl oxalate to form oxalyldiacetone, ethyl acetoneoxalate, or ethyl acetonedioxalate, according to the experimental conditions, and since substituted acetones, such as dibenzyl ketone, differ from acetone itself in forming cyclic triketones with ethyl oxalate, the authors have studied the condensation of methyl ethyl ketone with ethyl oxalate.

$\gamma\epsilon\zeta\theta$-*Decanetetrone*, $CH_2Me\cdot CO\cdot CH_2\cdot CO\cdot CO\cdot CH_2\cdot CO\cdot CH_2Me$, prepared by the condensation of methyl ethyl ketone with ethyl oxalate in the presence of sodium, is a yellowish-white solid and melts at 75—76°. Its solutions are intensely yellow. Its *dioxime* separates from alcohol in colourless leaflets and melts at 180°.

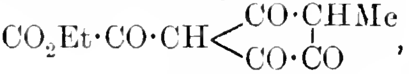
Ethyl propionylpyruvate, $CH_2Me\cdot CO\cdot CH_2\cdot CO\cdot CO_2Et$, prepared by the condensation of methyl ethyl ketone with ethyl oxalate in the presence of sodium ethoxide, boils at 73—78° under 0·6 mm. pressure; it is a faintly yellow oil with a characteristic odour. It forms sparingly soluble metallic salts, and gives a dark red coloration with ferric chloride. Its *sodium hydrogen sulphite additive compound*,

$$C_8H_{12}O_4,NaHSO_3,$$

crystallises in colourless leaflets.

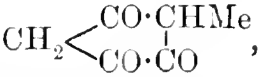
When heated at 120° with concentrated hydrochloric acid, ethyl propionylpyruvate forms *propionylpyruvic acid*, which separates from water in colourless crystals containing H_2O and melts at 63—65°; the anhydrous acid melts at 83·5°. The aqueous solution gives a dark red coloration with ferric chloride.

By variation of the conditions of the condensation of methyl ethyl ketone and ethyl oxalate in the presence of sodium ethoxide, *ethyl 1-methyl*cyclo*pentane-2 : 4 : 5-trione-3-glyoxylate*,



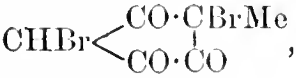
$$CO_2Et\cdot CO\cdot CH<\begin{array}{l}CO\cdot CHMe\\ CO\cdot CO\end{array},$$

is formed, melting at 161°; its solutions are strongly yellow. When saponified, it forms 1-*methyl*cyclo*pentane-2 : 4 : 5-trione-3-glyoxylic acid*,  $CO_2H\cdot CO\cdot CH<\begin{array}{l}CO\cdot CHMe\\ CO\cdot CO\end{array}$, which, when dehydrated, melts and decomposes at 193°; it separates from ethyl acetate in prismatic needles which are green and darker in colour than the ester. Its *dimethylaniline* salt melts at 151·5°.

1-*Methyl*cyclo*pentane-2 : 4 : 5-trione*,  $CH_2<\begin{array}{l}CO\cdot CHMe\\ CO\cdot CO\end{array}$, prepared by boiling the ethyl methyl*cyclo*pentanetrioneglyoxylate described with dilute hydrochloric acid, separates from water in colourless needles containing $1H_2O$, melts at 78·5—79·5°, or at 118° when dehydrated; its aqueous solution gives a red coloration with ferric chloride. Its *oxime* melts at 216—217°.

The proximity of two carbonyl groups in the molecule of the ketone is indicated by the formation with *o*-phenylenediamine of a normally constituted *quinoxaline* derivative, which melts indefinitely at about 317°.

The action of bromine on the ketone yields *dibromomethyl*cyclo*pentanetrione*,

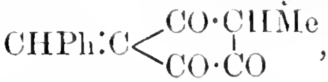


$CHBr{<}\begin{matrix}CO\cdot CBrMe\\ |\\ CO\cdot CO\end{matrix}$

, which crystallises in slightly coloured leaflets and melts at 182°. Like the parent ketone, it acts as a monobasic acid.

The *methyl ether* of the methyl*cyclo*pentanetrione melts at 51°.

The presence of an acid methylene group in the molecule of the ketone is shown by the action of benzaldehyde on the ketone, when the *benzylidene* derivative,



$CHPh{:}C{<}\begin{matrix}CO\cdot CHMe\\ |\\ CO\cdot CO\end{matrix}$

, is formed; it separates from methyl alcohol in yellow prisms and melts at 194—195°; its solution in alkalis is yellow; the benzylidene derivative forms an *aniline* salt which melts at 132°.

A. McK.

1 : 4-Anthraquinone. Kasimir Lagodzinski (*Ber.*, 1906, **39**, 1717—1718)—1-Anthrol combines with diazonium salts to form azo-compounds which are reduced in acid or alkaline solution to 1 : 4-aminoanthrol, the hydrochloride of which is oxidised by ferric chloride to 1 : 4-anthraquinone (Dienel, this vol., i, 290).

C. S.

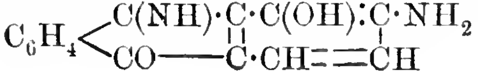
The Influence of Catalysts on Substitution in the Aromatic Nucleus. Karl Holdermann (*Ber.*, 1906, **39**, 1250—1258).—Attention is drawn to the influence which mercury salts and boric acid have on the sulphonation of anthraquinone (Dünschmann; Liebermann & Pleus, Abstr., 1904, i, 326; Farbenfabriken vorm. F. Bayer & Co., this vol., i, 293). Relatively large amounts of boric acid are required, and its influence is attributed to the formation of esters. Minute quantities of mercury salts, on the other hand, are sufficient.

The addition of small amounts of mercury on mercurous sulphate has no effect on the sulphonation of toluene, benzoic acid, or *α*-naphthol. The addition of mercury to a mixture of aniline and sulphuric acid produces oxidation rather than sulphonation, and if the temperature is kept at 125—130° small amounts of benzidine and a red oil are obtained. Reduced nickel and copper have no catalytic action on these preparations.

Mercury, copper, cobalt, and nickel have no effect on the nitration of toluene or nitrobenzene, but mercuric nitrate appears to have a considerable influence on the nitration of anthraquinone and its *β*-methyl derivative.

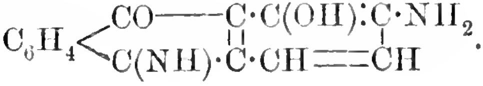
J. J. S.

Action of Ammonia on Alizarin. Roland Scholl and M. Parthey (*Ber.*, 1906, **39**, 1201—1206. Compare Prud'homme, this vol., i, 193; Noelting and Wortmann, *ibid.*, 291).—Perger's 1 : 2-diaminoanthraquinone (Abstr., 1879, 254, 724), formed by the action of concentrated aqueous ammonia on alizarin at 140° under pressure, is 2-amino-1-hydroxyanthraquinoneimide,

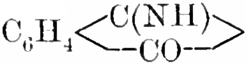


$C_6H_4{<}\begin{matrix}C(NH)\cdot C\cdot C(OH){:}C\cdot NH_2\\ \quad\ \ |\ |\qquad\qquad |\\ CO\text{——}C\cdot CH{=\!=}CH\end{matrix}$

or

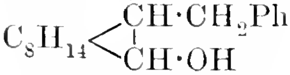


$C_6H_4{<}\begin{matrix}CO\text{——}C\cdot C(OH){:}C\cdot NH_2\\ \quad\ \ |\ |\qquad\qquad |\\ C(NH)\cdot C\cdot CH{=\!=}CH\end{matrix}$.

It commences to decompose and evolve ammonia at 250°, melts at about 280°, dissolves in dilute alkali hydroxides or acids, forming solutions from which it is reprecipitated on neutralisation, and when boiled with glacial acetic acid yields 2-acetylamino-1-hydroxyanthraquinone melting at 242°. The *potassium* derivative, $C_{14}H_9O_2N_2K,CH_4O$, was analysed. The *acetyl* derivative,  $C_6H_4{<}\begin{matrix}C(NH)\\ CO\end{matrix}{>}C_6H_2(OH)\cdot NHAc$, is obtained as a red, crystalline powder, which commences to decompose at 225°.

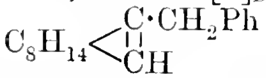
Liebermann's alizarinimide and ammonium derivative of alizarinimide (this Journal, 1877, i, 613) are identical with 2-amino-1-hydroxyanthraquinone and 2-amino-1-hydroxyanthraquinoneimide respectively. G. Y.

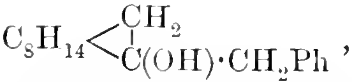
Preparation of Borneol and Bornyl Acetate from Pinene Hydrochloride. JOSEF HOUBEN (*Ber.*, 1906, **39**, 1700—1702. Compare Abstr., this vol., i, 21).—A current of dry air or oxygen is passed through the ethereal solution containing the product of the reaction between pinene hydrochloride, magnesium, and a trace of methyl iodide; subsequent treatment with ice and sulphuric acid or with ice and acetic anhydride yields borneol or bornyl acetate respectively. C. S.

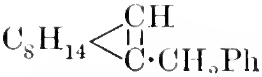
Benzyl- and Phenyl-borneols and their Products of Dehydration, Benzyl- and Phenyl-camphenes. ALBIN HALLER and E. BAUER (*Compt. rend.*, 1906, **142**, 677—681).—*a-Benzylborneol*,  $C_8H_{14}{<}\begin{matrix}CH\cdot CH_2Ph\\ |\\ CH\cdot OH\end{matrix}$, prepared by reducing benzylcamphor or benzylidenecamphor by means of sodium and alcohol, is a viscous oil which boils at 179—181° under 13 mm. pressure, has a sp. gr. 1·1325 at 18°/4°, and $[a]_D + 26°10'$; the *phenylurethane* crystallises in white crusts from a mixture of ether and light petroleum, melts at 116—118°, and has $[a]_D - 21°17'$; the *hydrogen phthalate*,

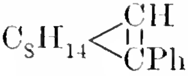
$$C_8H_{14}{<}\begin{matrix}CH\cdot CH_2Ph\\ |\\ CH\cdot O\cdot CO\cdot C_6H_4\cdot CO_2H\end{matrix},$$

is crystalline, melts at 146°, and has $[a]_D + 46°8'$.

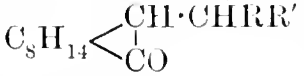
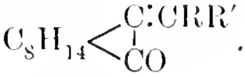
a-Benzylcamphene,  $C_8H_{14}{<}\begin{matrix}C\cdot CH_2Ph\\ ||\\ CH\end{matrix}$, is formed when a-benzylborneol is dehydrated by means of phthalic anhydride, anhydrous formic acid, or pyruvic acid (compare Bouveault and Blanc, Abstr., 1905, i, 222); it boils at 170—171° under 20 mm. pressure or 160—161° under 10 mm. pressure, but the specific rotation varies in the different preparations, being 8°20', 5°20', or 1°25', according as phthalic anhydride, formic acid, or pyruvic acid is the dehydrating agent employed.

β-Benzylborneol,  $C_8H_{14}{<}\begin{matrix}CH_2\\ |\\ C(OH)\cdot CH_2Ph\end{matrix}$, formed by the action of magnesium phenyl bromide on camphor, is an oil which boils at 169—170° under 10 to 11 mm. pressure, has $[a]_D - 12°0'$, forms a crystalline derivative with formic acid, and yields *β-benzylcamphene*,

 $C_8H_{14}<\begin{array}{l}CH\\ \|\\ C\cdot CH_2Ph\end{array}$, when dehydrated by means of pyruvic acid, anhydrous formic acid, or phthalic anhydride. This hydrocarbon forms white needles, melts at 24°, boils at 150—161° under 11 mm. pressure, has $[\alpha]_D$ −60°44′, forms a white crystalline additive compound with hydrogen bromide, which melts at 63—64°, and is oxidised by potassium permanganate, forming a mixture of benzoic and camphoric acids.

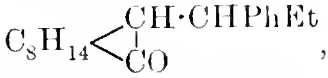
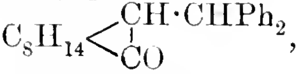
β-Phenylborneol,  $C_8H_{14}<\begin{array}{l}CH_2\\ |\\ CPh\cdot OH\end{array}$, prepared in a similar manner to the corresponding benzyl compound, is a crystalline compound which melts at 40—41° and boils at 157—158° under 12 mm. pressure; when dehydrated by means of pyruvic acid, it yields *β-phenylcamphene,*  $C_8H_{14}<\begin{array}{l}CH\\ \|\\ CPh\end{array}$, which is an oil boiling at 138—141° under 10 mm. pressure, and having a sp. gr. 0·9736 at 18°/11° and $[\alpha]_D$ +7°15′.

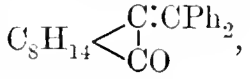
M. A. W.

Diphenyl- or Alkylphenyl-camphoryl-methanes and -methylenes,  $C_8H_{14}<\begin{array}{l}CH\cdot CHRR'\\ |\\ CO\end{array}$ and  $C_8H_{14}<\begin{array}{l}C:CRR'\\ |\\ CO\end{array}$.

ALBIN HALLER and E. BAUER (*Compt. rend.*, 1906, **142**, 971—976).—Benzylidenecamphor reacts with organo-magnesium derivatives to form the corresponding substituted phenylcamphorylmethanes, and the following compounds were thus prepared. *Phenylmethylcamphorylmethane,*

$$C_8H_{14}<\begin{array}{l}CH\cdot CHPhMe\\ |\\ CO\end{array},$$

forms white crystals melting at 70—71°, and soluble in alcohol or benzene. *Phenylethylcamphorylmethane,*  $C_8H_{14}<\begin{array}{l}CH\cdot CHPhEt\\ |\\ CO\end{array}$, forms white crystals melting at 80°. *Phenylbenzylcamphorylmethane,*  $C_8H_4<\begin{array}{l}CH\cdot CHPh\cdot CH_2Ph\\ |\\ CO\end{array}$, forms a thick oil boiling at 230° under 10 mm. pressure and has $[\alpha]_D$ +90°49′ in absolute alcohol. *Diphenylcamphorylmethane,*  $C_8H_{14}<\begin{array}{l}CH\cdot CHPh_2\\ |\\ CO\end{array}$, forms well-defined white crystals melting at 106—107° and has $[\alpha]_D$ +62°; the same compound is also obtained by reducing diphenylcamphorylmethylene (see below) with sodium amalgam, but the specific rotation of the compound thus prepared varies from +80°10′ to 40°29′.

Diphenylcamphorylmethylene,  $C_8H_{14}<\begin{array}{l}C:CPh_2\\ |\\ CO\end{array}$, obtained by the action of benzophenone on the sodium derivative of camphor, boils at 250° under 15 mm. pressure, and crystallises from a mixture of ether and light petroleum in the form of magnificent yellow octahedra, which melt at 113·5°; it has $[\alpha]_D$ +287° in alcoholic solution; the same compound is also obtained as a by-product in the preparation of diphenylcamphorylcarbinol, which has $[\alpha]_D$ +62°49′ (Malmgren, Abstr., 1903, i, 103, 711), or by the dehydration of the carbinol by means of anhydrous formic acid or pyruvic acid; the chief product of the latter reaction is, however, a *compound*, $C_{23}H_{26}O_2$, which forms a white solid melting at 200°. M. A. W.

The Pinene Fractions of French and American Turpentine Oils. BERTEL AHLSTRÖM and OSSIAN ASCHAN (*Ber.*, 1906, **39**, 1441—1446).—Ten or eleven fractions, collected from French and American turpentine respectively between 153° and 175°, showed continual diminution in rotatory power, accompanied in the latter case by change of sign. From a comparison of the rotations of the hydrochlorides of these fractions, the author considers that the two oils contain a common constituent, which is possibly nopinene (Semmler's pseudopinene, Abstr., 1900, i, 452). The yield of nopinic acid is about fifteen times as great from the higher-boiling as from the lower-boiling fractions of American turpentine. C. S.

Terpenes from Finnish Pine and Fir Resins. OSSIAN ASCHAN (*Ber.*, 1906, **39**, 1447—1451. Compare Aschan and Hjelt, Abstr., 1895, i, 545).—The resin from Finland pine, *Pinus sylvestris*, gives 9·2 per cent. of terpenes boiling below 180°, from which pinene and sylvestrene have been isolated. The fraction 155—160° has a sp. gr. 0·8657 and $[\alpha]_D + 20·22°$.

The resin from the fir, *Pinus abies*, contains only 4·5 per cent. of terpenes. The fraction 155—160° has $[\alpha]_D - 7·87°$, and *l*-pinene and also *l*-limonene have been isolated, the latter in the form of dipentene dihydrochloride. Sylvestrene could not be detected. J. J. S.

Patchouli and Citronella Oils from Perak, Federated Malay States (*Bull. Imp. Inst.*, 1905, **3**, 228—230).—The patchouli oil was dark lemon-yellow, had a sp. gr. 0·9525, n_D 1·5063, $\alpha_D - 43°31'$ in a 100 mm. tube, and was soluble in 90 per cent. alcohol to the extent of one volume in 7·4 volumes.

The citronella oil was pale yellow, had a sp. gr. 0·8948 at 15°, n_D 1·4858 at 24°, $\alpha_D - 1°34'$ at 24° in a 100 mm. tube, and was soluble in an equal volume of 80 per cent. alcohol. It contained 32·7 per cent. of geraniol and 55·3 per cent. of citronellal. E. G.

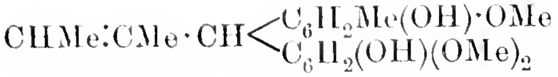
Guaiacum Resin. PAUL RICHTER (*Arch. Pharm.*, 1906, **244**, 90—119).—When submitted to dry distillation under 22 mm. pressure, the resin yielded 60 per cent. of distillate, boiling at 80—270°, whilst porous, shining charcoal remained in the retort. By means of distillation with steam, solution in aqueous sodium hydroxide, and fractional distillation, there were isolated from the distillate: tiglic aldehyde, guaiacol, cresol, pyroguaiacol, and a *substance* which boiled at 255—260° under 4 mm. pressure, resinous in character at first, but yielding crystals by slow evaporation of its solution in benzene and light petroleum. This melts at 107°, has the composition $C_{19}H_{20}O_5$, dissolves in aqueous alkali hydroxides but not in alkali carbonates, forms a *dibenzoyl* derivative melting at 143°, and is not affected by fusion with potassium hydroxide.

Guaiaconic acid was submitted to dry distillation very slowly under 22 mm. pressure. It yielded upwards of 60 per cent. of distillate at 80—280°, from which there were isolated: tiglic aldehyde, guaiacol, the substance described above melting at 107°, a crystalline *substance*, $C_{16}H_{18}O_3$, melting at 133°, and soluble in aqueous alkali hydroxides but not in alkali carbonates, and a resinous *substance*, $C_{34}H_{38}O_7$, which boils at 270—273° under 22 mm. pressure, dissolves in aqueous alkalis, but not in alkali carbonates, forms a powdery *tribenzoyl* derivative, which melts at 77—78° and is insoluble in aqueous alkalis, and gives a blue coloration with oxidising agents. In another experiment, where the guaiaconic acid was distilled under 22 mm. pressure as rapidly as possible, it yielded 65 per cent. of distillate, from which there were isolated: tiglic aldehyde, guaiacol, a small quantity of a crystalline *substance* melting at 203°, a syrupy *substance*, $C_{14}H_{16}O_4$, which boils at 170—174° under 22 mm. pressure, dissolves in aqueous alkali hydroxides, forms a crystalline *dibenzoyl* derivative melting at 103°, darkens in the air, and gives a green coloration with alcoholic ferric chloride, pyroguaiacol, and the substance described above as boiling at 270—273° under 22 mm. pressure.

Guaiaconic acid was isolated from guaiacum resin by extracting a mixture of the latter with sand with boiling benzene, concentrating the extract, and precipitating it with light petroleum. The precipitate was mixed with sand and extracted with ether, to which chloroform was added as the extraction progressed, the extract was then run in a thin stream into light petroleum. The guaiaconic acid thus precipitated was dissolved in benzene and the solution set aside. From the solution, *β-guaiaconic acid,* $C_{21}H_{26}O_5$, crystallised in small rhombohedra; this melts at 127°, forms a *dibenzoyl* derivative which melts at 138°, is insoluble in aqueous alkali hydroxides, and is not converted by oxidising agents into any blue substance. The benzene mother liquor contained *α-guaiaconic acid,* $C_{22}H_{26}O_6$ or $C_{22}H_{24}O_6$, which was obtained as a light powder by pouring a solution of it in ether and chloroform into light petroleum; it melts at 73° to a green liquid which turns brown at 101°, forms a *tribenzoyl* derivative which melts at 133—135°, is insoluble in aqueous alkalis, changes to a blue substance in the air or under the influence of oxidising agents, and when boiled with sulphurous acid retains the same composition, but melts at 101° to a brown liquid, without first turning green at 71°. Operations with this substance and with the crude guaiaconic acid were conducted in the dark.

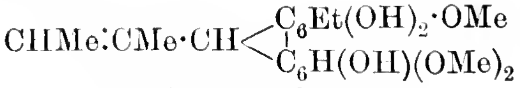
Guaiacum-blue, $C_{22}H_{24}O_9$, was obtained by shaking a 5 per cent. chloroform solution of α-guaiaconic acid with lead dioxide, added a little at a time, filtering the solution, and evaporating it under diminished pressure. It forms a dark blue powder; it is reduced by sulphurous acid at 50° to α-guaiaconic acid melting at 99—101° to a brown liquid without first turning green at 72°; when heated at 100°, it loses oxygen and leaves a brown residue, $C_{22}H_{24}O_7$, which melts at 85° and is converted into the blue substance by oxidising agents when heated at 120°, it leaves a residue of α-guaiaconic acid.

The following constitutional formulæ are suggested:



$$CHMe{:}CMe\cdot CH\begin{cases}C_6H_2Me(OH)\cdot OMe\\ C_6H_2(OH)(OMe)_2\end{cases}$$

β-Guaiaconic acid, $C_{21}H_{26}O_5$.



$$CHMe{:}CMe\cdot CH\begin{cases}C_6Et(OH)_2\cdot OMe\\ C_6H(OH)(OMe)_2\end{cases}$$

α-Guaiaconic acid, $C_{22}H_{26}O_6$.

C. F. B.

Effect of Heat on the Toxicity of Bitter Almonds. Giuseppe Velardi (*Chem. Centr.*, 1906, i, 1030; from *Boll. Chim. Farm.*, **45**, 65—67).—The following experiments on the effect of heat on the action of the emulsin on the amygdalin in bitter almonds were suggested by a case of poisoning. Whole and sliced almonds were heated in an air-bath at a constant temperature for two hours; they were then boiled with water and the distillate tested for hydrocyanic acid by means of the Prussian-blue reaction. It was found that at temperatures below 103° hydrocyanic acid was formed, but that at 105° the whole almonds alone showed the presence of a trace. At temperatures above 105°, hydrocyanic acid was not liberated, but the acid was formed when the almonds were macerated with powdered sweet almonds. Above 150°, hydrocyanic acid was only formed after several hours, and at 166° a day's heating was required. In all the experiments, the whole almonds withstood the action of heat better than the cut almonds and were found to contain a trace of hydrocyanic acid even after heating at 170°.

Pure amygdalin from Schuchardt melted at 208—210° when rapidly heated, but when slowly heated began to turn brown at 170° and melted at 180°, forming a resinous mass which contained 4·09 per per cent. of nitrogen and was soluble in water, but only sparingly so in 65 per cent. alcohol; when treated with powdered sweet almonds and water, hydrocyanic acid was formed. The sample of amygdalin before heating contained 2·96 per cent. of nitrogen. Since a temperature of 170° is required to render the amygdalin incapable of being attacked by ferments, it is necessary to heat to this temperature to destroy the toxicity of bitter almonds. E. W. W.

Preparation of Blue and Violet Dyes by Oxidation. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 162625 and 162626).—Fast blue, violet, or in some cases black dyes are obtained by oxidising *p*-amino-, *p*-aminohydroxy-, or *p*-diamino-derivatives of diphenylamine, mixed with primary, secondary, or tertiary *m*-aminophenols, *m*-diamines, alkylated *m*-diamines, phenols, naphthols, hydroxycarboxylic acids, or *o*-aminophenol ethers. The components are mixed on the fibre with the oxidising agent, preferably a chlorate, and developed by heat. Acids are not added, salts such as aluminium chloride being preferable. Oxygen carriers, such as cerium salts, may or may not be added. C. H. D.

Certain Properties of Dye-bases and Dye-acids. Leonor Michaelis (*Beitr. chem. Physiol. Path.*, 1906, **8**, 38—50).—An aqueous solution of Nile-blue base may be obtained by the addition of a little alkali hydroxide to a very dilute solution of the sulphate of the base. Examination with the ultramicroscope proves that the solution is in reality a suspension, and exposure to sunlight rapidly causes the formation of visible particles. Pseudo-solutions of practically all thiazines and oxazines are coagulated by light in a similar manner.

When sodium hydroxide solution is added to an aqueous solution of methylene-azure hydrochloride, a blue or bluish-violet solution is obtained, which can be preserved in the dark for some time, but turns red on exposure to light, and ultimately deposits a precipitate. The action of light is of a permanent nature, as the red solution when acidified yields a blue solution which, on the addition of alkali, turns red even in the dark. The red product is termed *photoazure*, and is also formed when methylene-blue solution is made alkaline and then exposed to sunlight.

True aqueous solutions of dye-bases, either in the form of the free bases (for example, methylene-blue base) or as salts (methylene-blue or Nile-blue), readily dye sections of organs (kidney, liver, spleen, or lymph-glands), especially the nuclei of the cells, whereas toluene solutions of the dye-bases or their salts do not stain the nuclei. The protoplasm colorations thus obtained are not stable in the presence of alcohol, and the colorations produced by aqueous and xylene solutions of the dye-salts are different: the former dissolve in Canada balsam, the latter do not.

Aqueous and xylene solutions of eosin-acid have much the same effect on sections of organs. J. J. S.

Process of Dyeing Animal Textile Fibres. II. P. Gelmo and Wilhelm Suida (*Monatsh.*, 1906, **27**, 225—235. Compare Abstr., 1905, i, 714).—The proportion in which two specimens of wool were found to absorb ammonia, hydrochloric acid, and sulphuric acid should have been given in the previous paper (*loc. cit.*) as

$$NH_3 : 20HCl : 24H_2SO_4/2$$

and $NH_3 : 20HCl : 21H_2SO_4/2$ respectively, instead of 1 : 2 : 2·4 and 1 : 2 : 2·1. Wool has therefore stronger basic properties than was then supposed.

Samples of a wool were boiled with distilled water, dilute hydrochloric acid, dilute ammonia, and aqueous sodium carbonate for one, twenty-one, and sixty hours, thoroughly washed with water, and titrated with $N/10$ sulphuric acid, $N/10$ hydrochloric acid, and $N/10$ ammonia. The aqueous extract had an odour of hydrogen sulphide and ammonia, and contained organic substances of the nature of peptone. Ammonia, hydrochloric acid, and sulphuric acid, were absorbed in the following proportions: by the untreated wool, $NH_3 : 17{\cdot}3HCl : 20{\cdot}3H_2SO_4/2$; by the wool after treatment for one hour with water, $NH_3 : 8{\cdot}1HCl : 9{\cdot}3H_2SO_4/2$; with hydrochloric acid, $NH_3 : 3{\cdot}6HCl : 3{\cdot}8H_2SO_4/2$; with ammonia, $NH_3 : 8{\cdot}4HCl : 19{\cdot}1H_2SO_4/2$; or with sodium carbonate, $NH_3 : 9{\cdot}4HCl : 9{\cdot}9H_2SO_4/2$.

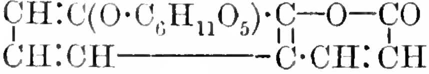
On further treatment of the wool with water, hydrochloric acid, or ammonia, its acidity increases only slowly, whilst even on prolonged boiling with water or ammonia the basicity remains unchanged. The increase of the acidity over the somewhat diminished basicity is more marked on prolonged treatment of the wool with hydrochloric acid. When the wool is boiled with aqueous sodium carbonate, the relation of the acidity to the basicity rapidly becomes constant.

After being boiled with water, ammonia, or dilute sodium carbonate, the wool behaves towards crystal-violet, or crystal-ponceau, in the same manner as before treatment, but the shades obtained on dyeing the treated wool with crystal-violet are slightly less fast, whilst those obtained on dyeing the wool, after treatment with hydrochloric acid, with crystal-violet or crystal-ponceau show little fastness to soaping.

When boiled with alcoholic sulphuric acid, wool forms a sulphate, as, after being washed thoroughly with water, it still retains sulphuric acid, which is removed entirely when the wool is boiled with ammonium carbonate.

Wool which has been treated with water, hydrochloric acid, ammonia, or aqueous sodium carbonate gives more intense colorations with diazobenzenesulphonic acid (Pauly and Binz, Abstr., 1905, i, 75) and with Millon's reagent than does the untreated wool. This points to an increase of phenolic hydroxyl groups during the treatment, and, with the other facts described, is explained by assuming the presence of lactone groups, R·CO·O·R′, in wool. G. Y.

Constitution of Tannins. MAXIMILIAN NIERENSTEIN (*Chem. Centr.*, 1906, i, 940—941; from *Collegium*, 1906, 45—49. Compare Abstr., 1905, i, 914).—The tannins are assumed to be derived from a hypothetical parent substance, tannone, COPh·OPh, tannin itself being regarded as pentahydroxytannonecarboxylic acid. Some evidence as to the group which confers the "tannoid" character on the tannins is afforded by the fact that gallic acid gives a precipitate with sodium chloride and gelatin. Salicylic, protocatechuic, 2 : 4-dihydroxybenzoic and vanillic acids and the methyl ether of 2 : 4-dihydroxybenzoic acid, the methyl, dimethyl, and trimethyl ethers of gallic acid, and the 4-methyl ether of gallic acid (compare Graebe and Martz, Abstr., 1903, i, 262) also give this reaction, whilst resorcinol, phloroglucinol, methyl gallate, methyl protocatechuate, and methyl 2 : 4-dihydroxybenzoate do not. The precipitation of gelatin is thus caused by the carboxyl group, but aromatic hydroxycarboxylic acids are not therefore to be regarded as tannins. That the CO group has a tannaphore character is also shown by the fact that whilst hexahydroxyaurincarboxylic acid precipitates gelatin, the hexahydroxydiphenylmethanedicarboxylic acid which is formed simultaneously (compare Kunz-Krause, Abstr., 1897, i, 530) does not. The glucotannoids, caffetannic acid,



$$\begin{array}{l}\mathrm{CH{:}C(O{\cdot}C_6H_{11}O_5){\cdot}C{-}O{-}CO}\\ \mathrm{CH{:}CH{-}{-}{-}{-}C{\cdot}CH{:}CH}\end{array}$$

and fabiantannic acid,

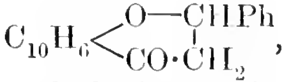
$$\begin{array}{l}\mathrm{C_6H_{11}O_5{\cdot}O{\cdot}C{:}CH{\cdot}C{\cdot}O{-}CO}\\ \mathrm{OMe{\cdot}C{:}CH{\cdot}C{\cdot}CH{:}CH}\end{array}$$

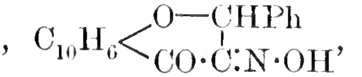
, contain a tannaphore CO group. A CO group of this character is also present in fustintannic, morintannic, and ellagotannic acids, the constitution of which is uncertain. E. W. W.

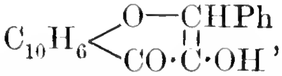
Dimethylpyrone Methiodide. Friedrich Kehrmann and Alfred Duttenhöfer (*Ber.*, 1906, 39, 1299—1304).—When a mixture of molecular amounts of dimethylpyrone and methyl sulphate is left at the ordinary temperature for several weeks, and a saturated aqueous solution of potassium iodide is then added to a solution of the product in little water, *dimethylpyrone methiodide*, $C_8H_{11}O_2I$, separates. It forms yellowish-white, glistening needles, and is slightly acid towards litmus. When its solution in water or in ethyl alcohol is heated, or when the solid is heated quickly above 100°, methyl iodide is evolved.

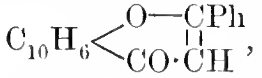
Dimethylpyrone methochloride platinichloride, $(C_8H_{11}O_2Cl)_2,PtCl_4$ prepared by the addition of an excess of sodium platinichloride to the concentrated aqueous solution of dimethylpyrone methosulphate, evolves methyl chloride when quickly heated at 158°. When its aqueous solution is boiled for several minutes and then cooled, a portion of the original substance separates in orange-coloured leaflets, whilst the remainder is converted into dimethylpyrone platinichloride.

A. McK.

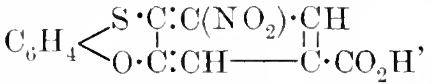
α-Naphthaflavonol. Gertrud Woker (*Ber.*, 1906, 39, 1649—1653).—α-*Naphthaflavanone*,  $C_{10}H_6<\begin{array}{l}O{-}CHPh\\ CO\cdot CH_2\end{array}$, prepared by heating the corresponding chalkone in alcoholic solution with hydrochloric acid (compare Kostanecki, Lampe, and Tambor, Abstr., 1904, i, 441), separates from alcohol in prisms and melts at 126°. The solution in alcohol is colourless, but exhibits a bluish-violet fluorescence.

Its iso*nitroso*-derivative,  $C_{10}H_6<\begin{array}{l}O{-}CHPh\\ CO\cdot C{:}N\cdot OH\end{array}$, prepared by the action of amyl nitrite on the preceding compound, crystallises from alcohol in glistening, yellow leaflets and melts at 173—174°. Its solution in alcohol is yellowish-red and exhibits a green fluorescence.

α-*Naphthaflavonol*,  $C_{10}H_6<\begin{array}{l}O{-}CHPh\\ CO\cdot C\cdot OH\end{array}$, prepared by hydrolysing the preceding compound with dilute sulphuric acid, separates from alcohol in green, iridescent leaflets and melts at 210°. It exhibits a marked fluorescence. Its *acetyl* derivative crystallises from alcohol in glistening leaflets and melts at 194—195°.

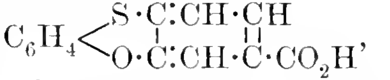
α-Naphthaflavone,  $C_{10}H_6<\begin{array}{l}O{-}CPh\\ CO\cdot CH\end{array}$, prepared by replacing a hydrogen atom in the α-position in α-naphthaflavanone by bromine and then acting on the resulting bromo-compound with alkali, melts at 154—156° and is identical with the compound prepared by Kostanecki by the aid of 2-benzylideneaceto-1-naphthol. α-*Bromonaphthaflavanone* separates from alcohol in crystals with a cauliflower-like appearance and melts at 134°.

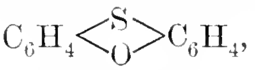
A. McK.

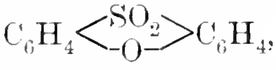
Phenothioxins and Naphthathioxins. Ferdinand Mauthner (*Ber.*, 1906, 39, 1340—1347. Compare Abstr., 1905, i, 461).—The monosodium derivative of *o*-dihydroxydiphenyl disulphide is reduced by sodium amalgam, neutralised, and a solution of 4-chloro-3 : 5-dinitrobenzoic acid in ethyl alcohol added. On addition of sodium hydroxide and decomposition of the resulting sodium salt with mineral acid, 4-*nitrophenothioxin-2-carboxylic acid*,  $C_6H_4<\begin{array}{l}S\cdot C{:}C(NO_2)\cdot CH\\ O\cdot C{:}CH\text{——}C\cdot CO_2H\end{array}$, is formed ; it separates from glacial acetic acid in orange-red needles and melts at 262°. Its *dioxide*, $C_{13}H_7O_7NS$, formed by oxidation with chromic acid in glacial acetic acid solution, separates from aqueous methyl alcohol in yellow needles and melts at 296—297°. The *mono-oxide*, $C_{13}H_7O_6NS$, formed by oxidation with dilute nitric acid of sp. gr. 1·2, separates from ethyl alcohol in yellow needles and melts at 251—252°.

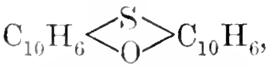
2′ : 4′-*Dinitro-2-hydroxydiphenylsulphide-6′-carboxylic acid*,
$C_{13}H_8O_7N_2S$,
prepared from *o*-dihydroxydiphenyl disulphide, 2-chloro-3 : 5-dinitrobenzoic acid, and sodium hydroxide, crystallises from xylene in yellow needles and melts at 216—217°.

4-*Aminophenothioxin-2-carboxylic acid*, prepared by the reduction of the corresponding nitro-acid with sodium sulphide in alcoholic solution, separates from dilute alcohol in colourless needles and melts and decomposes at 250°. Its salts are completely hydrolysed when boiled with water. Its *acetyl* derivative separates from alcohol in colourless needles and melts and decomposes at 294—295°.

Phenothioxin-2-carboxylic acid,  $C_6H_4<\begin{array}{l}S\cdot C{:}CH\cdot CH\\ O\cdot C{:}CH\cdot C\cdot CO_2H\end{array}$, prepared by eliminating the amino-group from 4-aminophenothioxin-2-carboxylic acid by the diazo-reaction, crystallises in colourless needles and melts at 223°. Its solution in concentrated sulphuric acid is red, but becomes colourless on the addition of water. When its calcium salt is submitted to dry distillation, it forms *phenothioxin*,


$$C_6H_4<\begin{array}{c}S\\ O\end{array}>C_6H_4,$$

which separates from alcohol in colourless needles and melts at 60—61° ; its solution in concentrated sulphuric acid is violet. Its *dioxide*,  $C_6H_4<\begin{array}{c}SO_2\\ O\end{array}>C_6H_4$, prepared by oxidising it with chromic acid in glacial acetic acid solution, separates from a mixture of benzene and light petroleum in colourless needles and melts at 140—141°. Its solution in concentrated acid is blue and becomes colourless on the addition of water.

Naphthathioxin,  $C_{10}H_6<\begin{array}{c}S\\ O\end{array}>C_{10}H_6$, prepared by the action of phosphorus oxychloride on β-dihydroxy-α-dinaphthyl sulphide, separates from glacial acetic acid in yellow needles and melts at 165—166°. Its solution in warm concentrated sulphuric acid is violet, and on dilution with water becomes colourless. Its *oxide*, $C_{20}H_{12}O_2S$, prepared by oxidising it with chromic acid in glacial acetic acid solution, forms reddish-yellow needles which melt and decompose at 220°. Its solution in concentrated sulphuric acid is green and becomes colourless on the addition of water.

A. McK.

Morphine. VII. Conversion of Thebaine into Codeinone and Codeine. LUDWIG KNORR and HEINRICH HÖRLEIN (*Ber.*, 1906, **39**, 1409—1414. Compare Abstr., 1903, i, 849).—When thebaine is hydrolysed by normal sulphuric acid for six to seven minutes at the boiling point or for seventeen days at the ordinary temperature, codeinone is obtained in small quantities. It is detected by its characteristic behaviour during fusion, and in the form of the oxime (*loc. cit.*). C. S.

Degradation of Hydroxycodeine by Exhaustive Methylation. LUDWIG KNORR and WILHELM SCHNEIDER (*Ber.*, 1906, **39**, 1414—1420). —Hydroxycodeine forms a *picrate*, $C_{18}H_{21}O_4N,C_6H_3O_7N_3$, which sinters and melts at 166°, and a *picrolonate*, $C_{18}H_{21}O_4N,C_{10}H_8O_5N_4$, which turns brown at 170° and melts and decomposes at 176°.

Hydroxymethylmorphimethine, $C_{19}H_{23}O_4N$, obtained by the action of sodium hydroxide on a boiling aqueous solution of hydroxycodeine methiodide, separates as a viscous oil, and, after purification from ether, forms long, colourless, glassy needles containing 1 mol. of the solvent, which is lost between 50° and 60°, the syrup being regenerated. The *hydrochloride*, $C_{19}H_{23}O_4N,HCl$, separates from alcohol in long needles containing alcohol of crystallisation, and, when dried, melts and decomposes at 246°. The *picrate* melts at 211°; the *picrolonate* sinters at 140° and melts indefinitely. The *methiodide* crystallises from water in needles containing $1\frac{1}{4}H_2O$, and decomposes when anhydrous at 220°. The *di-acetate* melts indefinitely at 81° and forms a *methiodide*, which decomposes at 260°. A 10 per cent. alcoholic potash solution at 100° converts hydroxymethylmorphimethine into a base, which melts indefinitely at 130° and yields a methiodide decomposing at about 300°. From these properties, the base appears to be β-methylmorphimethine (Abstr., 1902, i, 817).

Hydroxymethylmorphimethine decomposes when heated with acetic anhydride, yielding ethanoldimethylamine and a *trihydroxydiacetylmethylphenanthrene*, $C_{19}H_{16}O_5$, which separates from alcohol in needles, melts at 201°, and is therefore not identical with the isomeride obtained from codeinone. C. S.

Action of Xanthine Leucomaines [Ptomaines] on Copper. N. SLOMNESCO (*Compt. rend.*, 1906, **142**, 789—790).—Theobromine, theophylline, or carbamide precipitates the yellow hydroxide of copper from solutions of the salts, and the author is of opinion that this property of the xanthine bases of the organism renders small quantities of copper non-toxic. M. A. W.

Xanthine Bases. ERNST SCHMIDT [and W. SCHWABE] (*Chem. Centr.*, 1906, i, 1241—1242; from *Apoth. Zeit.*, **21**, 213—214. Compare Bergell and Richter, Abstr., 1905, ii, 744).—Most of the following alkyltheophyllines were prepared from potassiumtheophylline in presence of alcohol, but a few were obtained by the action of the alkyl iodide on silvertheophylline. *Ethyltheophylline*, $C_7H_7EtO_2N_4$, crystallises in white needles, melts at 154°, and is readily soluble in hot water, but somewhat less so in cold; the *hydrochloride*,

$$C_7H_7EtO_2N_4,HCl,2H_2O,$$

the *hydrobromide*, and the *sulphate* form white needles and are decomposed by water. The *aurichloride*, $C_7H_7EtO_2N_4,HAuCl_4,H_2O$, crystallises in yellow needles and melts at 224°; the *platinichloride* forms reddish-yellow plates and melts at about 274°. Compounds are also formed with mercuric chloride, mercuric cyanide, silver nitrate, methyl chloride, and methyl iodide, but attempts to prepare an ethiodide failed.

Propyltheophylline and *isopropyltheophylline* crystallise in needles and are readily soluble in water; they melt at 99—100° and 140° respectively. *Benzyltheophylline* crystallises in white needles which resemble those of caffeine; it melts at 158° and is very sparingly soluble in water. The *aurichloride* forms yellow needles and melts at 104°; the *platinichloride* forms reddish-yellow needles and melts about 250°.

E. W. W.

Compound of Lithium with Theobromine. ERNEST DUMESNIL (*J. Pharm. Chim.*, 1906, [vi], **23**, 326—328).—A soluble lithium-theobromine compound is obtained by adding an excess of theobromine to a solution of lithium oxide, filtering the mixture, and evaporating the filtrate under reduced pressure over sulphuric acid. The residue is afterwards dried at 110° under reduced pressure. The product obtained has a composition corresponding with the formula $C_7H_7O_2N_4Li$, the lithium replacing one hydrogen atom in the theobromine molecule. Lithium-theobromine forms fine needle-like crystals and is soluble in less than half its own weight of water. The solution becomes turbid on exposure to the air owing to the formation of lithium carbonate and free theobromine.

W. P. S.

Dichlorotetrapyridinecobalt Salts. ALFRED WERNER and RUDOLF FEENSTRA (*Ber.*, 1906, **39**, 1538—1545).—Dichlorotetrapyridinecobalt salts are formed by the action of aqueous pyridine on dichlorodiaquodiamminecobalt hydrogen sulphate, or, better, by oxidation with chlorine of cobalt chloride dissolved in aqueous pyridine solution. The salts are mostly greyish-green, but the bromide is an intense leaf-green, and the aurichloride is yellowish-green. The chlorine atoms of the dichlorotetrapyridinecobalt nucleus are not removed by prolonged treatment with water at the ordinary temperature, and cannot be substituted by nitrito- or thiocyano-groups. The action of ammonia on the salts leads to the formation of chloropenta-amminecobalt chloride; when boiled with hydrochloric acid, the dichlorotetrapyridinecobalt salts yield cobaltous chloride.

Dichlorodiaquodiamminecobalt hydrogen sulphate is prepared best by the action of sulphuric acid on a cooled aqueous solution of dichlorodiaquodiamminecobalt chloride, which is formed by the action of chlorine on ammonium tetranitritodiamminecobalt dissolved in concentrated hydrochloric acid, cooled by ice.

Dichlorotetrapyridinecobalt chloride, $[Cl_2CoPy_4]Cl,6H_2O$, crystallises in shimmering leaflets, is bluish-green when anhydrous, and in 5 per cent. solution gives with potassium cobalticyanide a light green, crystalline precipitate which becomes red, with potassium dichromate a yellowish-brown, and with potassium ferrocyanide an emerald-green coloration, and with sodium nitroprusside a light green crystalline, with iron-alum a dirty-green, and with Erdmann's salt a yellowish-green precipitate. The *bromide*, $[Cl_2CoPy_4]Br$, formed by the action of potassium bromide on the chloride in aqueous solution, separates in small, glistening crystals, or from alcohol in light yellow needles. The *iodide* is obtained as a flocculent, brown precipitate which, when dried, decomposes with separation of iodine; the *thiocyanate* is unstable; the *nitrate*, $[Cl_2CoPy_4]NO_3,H_2O$, crystallises in slender needles; the *hydrogen sulphate*, $[Cl_2CoPy_4]HSO_4,2H_2O$, forms small leaflets and needles; the *platinichloride*, $[Cl_2CoPy_4]_2PtCl_6$, and the *aurichloride*, $[Cl_2CoPy_4]AuCl_4$, are obtained as crystalline precipitates. G. Y.

Synthesis of Pyridine Bases from Saturated Aldehydes and Ammonia.

ALEXEI E. TSCHITSCHIBABIN (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 1229—1253).—The author first discusses the work previously published on this subject, some of which he has repeated. His results show that, in all the cases investigated by him, the action of ammonia on aldehydes consists of a trimolecular condensation proceeding according to the equation:

$$3R\cdot CH_2\cdot CHO + NH_3 = CH\Big\langle\begin{matrix}CR{:}C(CH_2R)\\CR\text{———}CH\end{matrix}\Big\rangle N + H_2 + 3H_2O.$$

The structure of the compounds formed is similar to that ascribed by Dürkopf and Schlaugk (Abstr., 1888, 607) to the parvoline obtained by Waage (Abstr., 1888, 39; 1884, 172) by the interaction of propaldehyde and ammonia. Acetaldehyde and ammonia yield, besides aldehydecollidine, a small quantity of α-picoline.

The action of ammonia on *iso*valeraldehyde yields 3 : 5-di*iso*propyl-2-*iso*butylpyridine, to which Ljubavin (Abstr., 1873, 1023) gave the name valeritrine (compare Wischnegradsky, Abstr., 1880, 269). This is an extremely hygroscopic base boiling at 258—259° under 740 mm. pressure, and has the sp. gr. 0·8833 at 20°/0°, 0·8910 at 10°/0°, and 0·8981 at 0°/0°; its hydrochloride melts at 82° and its picrate at 133°. On reduction with sodium and alcohol, it yields *hexahydrovaleritrine*, $C_{15}H_{31}N$, which is a syrupy secondary base boiling at 265° and having sp. gr. 0·8556 at 20°/0°, 0·8625 at 10°/0°, and 0·8694 at 0°/0°; it rapidly absorbs carbon dioxide from the air. The *hydrochloride*,

$$C_{15}H_{31}N,HCl,$$

forms hexagonal needles melting at 286° and dissolves in alcohol or ether, and sparingly in water. The *platinichloride*,

$$(C_{15}H_{31}N)_2,H_2PtCl_6,$$

crystallises in microscopic, orange prisms melting and decomposing at 203°. The *picrate*, $C_{15}H_{31}N,C_6H_2(NO_2)_3\cdot OH$, crystallises from alcohol in small, shining prisms melting at 174°. The *acid oxalate*,

$$C_{15}H_{31}N,H_2C_2O_4,$$

separates in needles melting and decomposing at 225°. Oxidation of valeritrine by means of potassium permanganate yields pyridinecarboxylic acids.

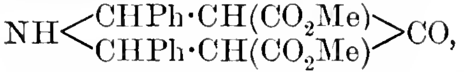
Ljubavin's hydrovaleritrine (*loc. cit.*) is either identical or isomeric with hexahydrovaleritrine.

The action of ammonia on *iso*valeraldehyde yields also a dimolecular condensation product, $C_{15}H_{27}N$, which is a tertiary base boiling at 170—175° under 25 mm. pressure; it was not obtained pure and yields no crystalline salts.

The interaction of ammonia and butyraldehyde gives rise to the formation of 3 : 5-diethyl-2-propylpyridine, $C_{12}H_{19}N$, which is a colourless oil boiling at 242° under 745 mm. pressure and has sp. gr. 0·9141 at 0°/0° and 0·9042 at 20°/0°. This base is formed by the condensation of 3 mols. of the aldehyde with 1 mol. of ammonia, and probably forms one constituent of Schiff's paradiconiine (Abstr., 1872, 416), which is most likely a mixture. On oxidising the base with potassium permanganate, it yields pyridine-2 : 3 : 5-tricarboxylic acid. T. H. P.

Condensation of Acetonedicarboxylic Esters with Benzaldehyde in the Presence of Ammonia. Pavel I. Petrenko-Kritschenko and N. Zoneff (*Ber.*, 1906, **39**, 1358—1361. Compare Abstr., 1900, i, 307).—The compounds previously described as substituted tetrahydropyrones are really derivatives of 4-piperidone.

Methyl-2 : 6-*diphenylpiperidone*-3 : 5-*dicarboxylate*,



$$NH<\begin{matrix}CHPh\cdot CH(CO_2Me)\\ CHPh\cdot CH(CO_2Me)\end{matrix}>CO,$$

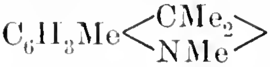
obtained by saturating an ice-cold mixture of benzaldehyde (2 mols.) and methyl acetonedicarboxylate (1 mol.) with dry ammonia, melts at 144—148° and develops an intense red coloration with ferric chloride. The *nitroso*-derivative, $C_{21}H_{20}O_5N\cdot NO$, melts at 148—149°. The *hydrochloride*, $C_{21}H_{21}O_5N,HCl$, is precipitated in 80 per cent. yield when hydrogen chloride is passed into a benzene solution of the ester.

Ethyl 2 : 6-*diphenylpiperidone*-3 : 5-*dicarboxylate*, $C_{23}H_{25}O_5N$, melts at 116—119°, and the *nitroso*-derivative at 147—150°; both give a red coloration with ferric chloride. The *hydrochloride*, $C_{23}H_{25}O_5N,HCl$, was also prepared.

A crystalline *potassium* derivative of the ethyl or of the methyl ester can be obtained most conveniently by the addition of alcoholic potassium hydroxide to a cold alcoholic solution of the ester, and is reconverted by boiling water into its generators. C. S.

Constitution of the Indoline Base formed from the *p*-Tolylhydrazone of Methyl *iso*Propyl Ketone. Arthur Konschegg (*Monatsh.*, 1906, **27**, 247—253. Compare Abstr., 1905, i, 924; Plancher, Abstr., 1898, i, 536; Plangger, Abstr., 1905, i, 718).—The acetyl derivative of 3 : 3 : 5-trimethyl-2-methyleneindoline is formed by the action of acetyl chloride on the base in presence of sodium acetate; it melts at 104° and is readily hydrolysed by aqueous alkali hydroxides.

The action of methyl iodide on 3 : 3 : 5-trimethyl-2-methyleneindoline in boiling methyl-alcoholic solution leads to the formation of a mixture of secondary and tertiary iodides, which crystallises in yellow prisms and melts at 229°. 2 : 3 : 3 : 5-*Tetramethyl*-ψ-*indole methiodide*,

 $C_6H_3Me{<}\begin{matrix}CMe_2—\\N(MeI)\end{matrix}{>}CMe$, which is thrown down on addition of ether to an alcoholic solution of the mixed iodides, crystallises in glistening, silky, slightly yellow needles and melts at 228°. 1 : 3 : 3 : 5-*Tetramethyl-2-methyleneindoline*,  $C_6H_3Me{<}\begin{matrix}CMe_2\\NMe\end{matrix}{>}C{:}CH_2$, is formed by the action of potassium hydroxide on the methiodide; it is a colourless oil, which distils at 134° under 10 mm. pressure, becomes red on exposure to air, and forms a *ferrichloride* and a *platinichloride*. The *picrate* crystallises in transparent, yellow plates and melts at 122°. G. Y.

Constitution of Thiazine and Oxazine Dyes. ARTHUR HANTZSCH (*Ber.*, 1906, **39**, 1365—1366. Compare this vol., i, 206).—A reply to Kehrmann (this vol., i, 306). C. S.

Conversion of Hydrazine Derivatives into Heterocyclic Compounds. XIX. Diacidylhydrazide Dichlorides. ROBERT STOLLÉ (*J. pr. Chem.*, 1906, [ii], **73**, 277—287. Compare Abstr., 1905, i, 249).—A *résumé* of the methods of preparing diacidylhydrazide dichlorides, R·CCl:N·N:CCl·R, and of their conversion into heterocyclic compounds. G. Y.

Oxidation of Diphenylamine. HEINRICH WIELAND and STEPHAN GAMBARJAN (*Ber.*, 1906, **39**, 1499—1506. Compare Wieland, Abstr., 1903, ii, 685; Baeyer, Abstr., 1905, i, 281).—Tetraphenylhydrazine is formed by the oxidation of diphenylamine with lead peroxide in benzene, or potassium permanganate in acetone, solution. When treated with concentrated sulphuric, aqueous, hydrochloric, or acetic acid, it is hydrolysed to diphenylamine and the salt of the hypothetical diphenylhydroxylamine, which is the source of the blue or violet coloration. If treated with hydrogen chloride in anhydrous ethereal solution, it gives an intense dark green coloration, which rapidly fades, and the resulting solution, after depositing diphenylamine hydrochloride, contains *p*-chlorodiphenylamine the product of isomeric change of diphenylhydroxylamine chloride. Tetraphenylhydrazine reacts in the same manner with hydrogen bromide.

Tetra-*p*-tolylhydrazine is formed by the oxidation of di-*p*-tolylamine with lead dioxide in benzene solution. With glacial acetic acid, it gives a more intense coloration than does tetraphenylhydrazine, and when treated with hydrogen chloride in ethereal solution cooled by ice gives a deep reddish-violet coloration, which fades only very slowly, di-*p*-tolylamine hydrochloride crystallising out. The coloured substance can be isolated as the *stannichloride*, which forms large, dark red crystals, and is decolorised rapidly on treatment with water; the ethereal solution gives intense colorations with acids.

When fused with phenol, tetraphenylhydrazine forms diphenylamine and a colourless compound (triphenylamine ?), no colour change being observed. Diphenylamine is formed also by reduction of tetraphenylhydrazine with zinc dust and glacial acetic acid.

Diphenylbenzidine (Kadiera, Abstr., 1905, i, 934) is formed together with the blue diphenylhydroxylamine sulphate by the action of concentrated sulphuric acid on tetraphenylhydrazine.

The action of concentrated sulphuric acid on a mixture of diphenylamine and *p*-hydroxydiphenylamine leads to the formation of 4-*hydroxydiphenylamine*-3-*sulphonic acid*, $NHPh\cdot C_6H_3(OH)\cdot SO_3H$, which crystallises in glistening scales, melts and decomposes at 290—291°, is insoluble in alcohol, gives an intense red coloration with ferric chloride, potassium dichromate, or permanganate in aqueous solution, and reduces silver nitrate and Fehling's solutions (compare Limpricht, Abstr., 1889, 397). G. Y.

Action of Pyridine on 1 : 5-Dichloro-2 : 4-dinitrobenzene.

Fritz Reitzenstein and Julius Rothschild (*J. pr. Chem.*, 1906, [ii], **73**, 257—276. Compare Reitzenstein, Abstr., 1903, i, 815; Zincke, Abstr., 1904, i, 448; 1905, i, 467; König, Abstr., 1904, i, 449, 817).—The moss-green compound, formed together with 2 : 4-dinitroaniline by the action of dinitrophenylpyridinium chloride on benzidine (Reitzenstein, *loc. cit.*), is found now to melt at 159—160°; it has the constitution

$$NH_2\cdot C_{12}H_8\cdot N:CH\cdot CH:CH\cdot CH:CH\cdot NH_2Cl\cdot C_{12}H_8\cdot NH_2.$$

The action of an excess of pyridine and 1-chloro-2 : 4-dinitrobenzene on aniline in alcoholic solution leads to the formation of the hydrochloride of the dianilide melting at 143° (Zincke, Heuser, and Möller, Abstr., 1904, i, 921), dinitrodiphenylamine melting at 155°, and dinitroaniline melting at 181—183°.

Dinitroaniline and dinitrophenylbenzidine, melting at 245°, are formed by the action of an excess of pyridine and 1-chloro-2 : 4-dinitrobenzene on benzidine in alcohol.

The red *dianilide*,

$$NH_2\cdot C_{12}H_6(SO_3H)_2\cdot N:CH\cdot[CH:CH]_2\cdot NH_2Cl\cdot C_{12}H_8(SO_3H)_2\cdot NH_2,H_2O,$$

is formed by the action of dinitrophenylpyridinium chloride on benzidinedi-*m*-sulphonic acid; it melts above 270° and does not dye wool or mordanted cotton-wool either in aqueous or alkaline solution.

The green *dianilide*,

$$NH_2\cdot C_{12}H_7(SO_3H)\cdot N:CH\cdot CH:CH\cdot CH:CH\cdot NH_2Cl\cdot C_{12}H_7(SO_3H)\cdot NH_2,$$

formed from benzidinesulphonic acid and dinitrophenylpyridinium chloride, melts at 245—255°.

The action of pyridine on 1 : 5-dichloro-2 : 4-dinitrobenzene leads to the formation of (*a*) the greenish-yellow condensation *product*, $C_6H_2(NO_2)_2<\begin{matrix}C_5NH_5\cdot O\\ C_5NH_5\cdot O\end{matrix}>C_6H_2(NO_2)_2$, which melts above 300°, dissolves in aniline or alkali hydroxides, and is readily soluble in dilute acids, and (*b*) *dinitrophenyldipyridinium dichloride*,

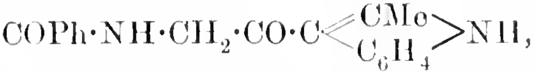
$$C_6H_2(NO_2)_2(C_5NH_5Cl)_2,$$

which crystallises from alcohol, melts at 147—148°, gives a green precipitate with sodium hydroxide, becoming reddish-brown on addition of acids, and when boiled with pyridine is converted into the condensation product.

When boiled with hydrochloric acid, the condensation product is decomposed, forming 2 : 4-dinitro-5-hydroxyphenylpyridinium hydroxide, $OH\cdot C_6H_2(NO_2)_2\cdot C_5NH_5\cdot OH$, which is obtained in glistening, red crystals melting at 208°. The yellow isomeric *additive* compound of pyridine and dinitroresorcinol, $C_6H_2(NO_2)(OH)_2,C_5NH_5$, melts at 111° and is decomposed into its components on treatment with dilute sodium hydroxide.

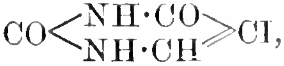
When heated on the water-bath with aniline in alcoholic solution, dinitrophenyldipyridinium dichloride forms the hydrochloride of the dianilide melting at 143° (Zincke, Heuser, and Möller, *loc. cit.*), together with 4 : 6-*dinitro*-1 : 3-*diaminobenzene*, $C_6H_2(NH_2)_2(NO_2)_2$, which separates in yellow crystals, melts above 300°, and is soluble in ethyl acetate.

With benzidine, benzidinedi-*m*-sulphonic acid, 4 : 4′-tetramethyldiamino-3″-amino-5″-methyltriphenylmethane, and 4 : 4′-tetramethyldiamino-3″-amino-2 : 2′ : 5″-trimethyltriphenylmethane, dinitrophenyldipyridinium dichloride yields the same dianilides, melting at 159—160°, above 270°, 115°, and 113° respectively, as are formed by dinitrophenylpyridinium chloride. G. Y.

Action of Hippuryl Chloride on 2-Methylindole. Emil Fischer and Carl Kaas (*Ber.*, 1906, **39**, 1276—1278).—3-*Hippuryl-2-methylindole*,  $\mathrm{COPh{\cdot}NH{\cdot}CH_2{\cdot}CO{\cdot}C}\left<\begin{matrix}\mathrm{CMe}\\ \mathrm{C_6H_4}\end{matrix}\right>\mathrm{NH}$, is formed when an intimate mixture of 2-methylindole, hippuryl chloride, and magnesium oxide is heated with dry benzene at 60—70°, while the whole is well shaken. It remains undissolved when the residue after filtration is extracted first with ether and then with dilute hydrochloric acid. It may be crystallised from glacial acetic acid or from alcohol, although only sparingly soluble in the latter. It begins to turn brown at 250°, melts and decomposes at about 269° (corr.), and dissolves sparingly in the ordinary organic solvents with the exception of glacial acetic acid.

When hydrolysed by heating at 100° with glacial acetic acid saturated with hydrogen chloride at 0°, it yields 3-*aminoacetyl-2-methylindole* (3-*glycyl-2-methylindole*),  $\mathrm{NH_2{\cdot}CH_2{\cdot}CO{\cdot}C}\left<\begin{matrix}\mathrm{CMe}\\ \mathrm{C_6H_4}\end{matrix}\right>\mathrm{NH}$, together with a complex compound melting at 190°. The glycyl compound forms small, colourless needles which, when moist, rapidly darken in contact with air. When rapidly heated, it melts and decomposes at 176° (corr.) and dissolves readily in dilute acids or in hot water, but only sparingly in warm benzene or toluene. It readily reduces Fehling's solution. J. J. S.

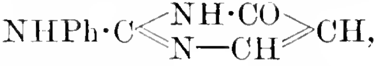
Derivatives of 5-Iodopyrimidine: 5-Iodocytosine. Treat B. Johnson and Carl O. Johns (*J. Biol. Chem.*, 1906, **1**, 305—318).—5-*Iodo*-6-*oxy-2-ethylthiolpyrimidine*,  $\mathrm{SEt{\cdot}C}\left<\begin{matrix}\mathrm{NH{\cdot}CO}\\ \mathrm{N{-}CH}\end{matrix}\right>\mathrm{CI}$, obtained by the action of an alkaline solution of iodine on 6-oxy-2-ethylthiolpyrimidine (Wheeler and Merriam, Abstr., 1903, i, 525), crystallises from alcohol in slender prisms melting at 196°. 5-*Iodouracil*,



$$\mathrm{CO}\left<\begin{matrix}\mathrm{NH{\cdot}CO}\\ \mathrm{NH{\cdot}CH}\end{matrix}\right>\mathrm{CI},$$

obtained from uracil in a similar manner, crystallises from water in glistening scales and decomposes at 272°.

5-*Iodocytosine*,  $\mathrm{CO}{<}\genfrac{}{}{0pt}{}{\mathrm{N{:}C(NH_2)}}{\mathrm{NH{-}{-}CH}}{>}\mathrm{CI}$, decomposes between 225° and 245°, evolving iodine. It is practically insoluble in alcohol or benzene, and its solubility in water is somewhat less than 1 in 1000. The *picrate*, $C_4H_4ON_3I,C_6H_3O_7N_3$, crystallises from hot water in long needles and decomposes between 247° and 257°. The *acetate* decomposes at 220—240° and dissociates when warmed with acetic acid.

6-*Chloro-5-iodo-2-ethylthiolpyrimidine*,  $\mathrm{SEt{\cdot}C}{<}\genfrac{}{}{0pt}{}{\mathrm{N{:}CCl}}{\mathrm{N{\cdot}CH}}{>}\mathrm{CI}$, obtained by the action of phosphorus oxychloride on the 5-iodo-derivative, crystallises from light petroleum in large prisms melting at 69°, and when heated with an alcoholic solution of ammonia at 128—130° yields 5-*iodo-6-amino-2-ethylthiolpyrimidine*, $C_6H_8N_3SI$, which crystallises from alcohol in slender prisms melting at 127°. When boiled with concentrated hydrochloric acid, the amino-compound is transformed quantitatively into 5-iodocytosine. 5-*Iodo-6-anilino-2-ethylthiolpyrimidine* is an oil, but yields a crystalline *sulphate*, $(C_{12}H_{12}N_3SI)_2,H_2SO_4$. 6-*Oxy-2-anilinopyrimidine*,  $\mathrm{NHPh{\cdot}C}{<}\genfrac{}{}{0pt}{}{\mathrm{NH{\cdot}CO}}{\mathrm{N{-}{-}CH}}{>}\mathrm{CH}$, obtained by warming 6-oxy-2-ethylthiolpyrimidine with the theoretical amount of aniline or by the action of aniline on 5-iodo-6-oxy-2-ethylthiolpyrimidine, crystallises from alcohol in well-developed plates, melts at 230—231°, and is insoluble in water or benzene. Ammonium hydroxide solution reacts in much the same manner as aniline and converts the iodo-derivative into 2-amino-6-oxypyrimidine, whereas alcoholic ammonia has no action. Aniline does not react with 5-iodo-6-amino-2-ethylthiolpyrimidine or with 5-iodocytosine. Alcoholic ammonia converts 5-iodocytosine into cytosine, and 5-iodouracil into uracil.

a-*Cyanobutyrylcarbamide*, $\mathrm{CN{\cdot}CHEt{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2}$, obtained by condensing α-cyanobutyric acid with carbamide, crystallises from water and melts at 181° with slight evolution of gas. When its solution in concentrated sodium hydroxide is kept for some hours and then neutralised with hydrochloric acid, 6-*amino-2:4-dioxy-5-ethylpyrimidine*,  $\mathrm{CO}{<}\genfrac{}{}{0pt}{}{\mathrm{N{:}C(NH_2)}}{\mathrm{NH{-}{-}CO}}{>}\mathrm{CHEt}$, is obtained. It crystallises from water in acicular prisms and decomposes at 339°.

The iodine atoms in the compounds described are firmly united to carbon, and the compounds do not react with the potassium salt of phthalimide or the sodium salt of urethane. J. J. S.

Preparation of Guanine. EMANUEL MERCK (D.R.-P. 162336).—2-Cyanoamino-4-amino-6-hydroxypyrimidine (Abstr., 1905, i, 670) forms an *iso*nitroso-derivative, which, on reduction, yields yellow needles of 2-*cyanoamino-4:5-diamino-6-hydroxypyrimidine*. When heated with 90 per cent. formic acid, the formate of the base at first crystallises out, but on boiling for several hours is converted into guanine formate, which may be decomposed by sodium hydroxide, yielding the base. C. H. D.

Stereochemistry of the 2 : 5-Diketopiperazines. Emil Fischer and Karl Raske (*Sitzungsber. K. Akad. Wiss. Berlin*, 1906, 371—383).—The A-isomeride of α-aminobutyryl-α-aminobutyric acid melts at 272—275° (corr.) under elimination of water and formation of an anhydride; it crystallises in glistening leaflets and forms a sparingly soluble copper salt; 5·4 grams of the acid dissolve in 100 grams of water at 24°. The B-isomeride melts at 260—262° (corr.), crystallises in short, obliquely cut, prismatic needles, and forms a soluble copper salt; 29 grams of the acid dissolve in 100 grams of water. On esterification and treatment with alcoholic ammonia, both isomerides are converted into anhydrides. A-diketodiethylpiperazine crystallises in long, narrow, obliquely cut plates aggregated in clusters, and melts at 277—278° (corr.) to a faintly brown liquid; 0·33 gram dissolves in 100 grams of water; the B-isomeride crystallises in thin, obliquely cut prisms generally badly formed, and melts to a faint brown liquid at 266—267° (corr.); 100 grams of water dissolve 1·03 grams of the acid. The anhydride formerly prepared by heating either the A- or B-dipeptides melts at 268—269° (corr.) and is regarded as a mixture.

Both A- and B-diketodiethylpiperazines when hydrolysed with alkali are converted into a dipeptide crystallising in small glistening plates, melting at 274—275° (corr.), forming a sparingly soluble copper salt, and dissolving in water to the extent of 5·2 grams per 100 grams of water.

l-*Bromopropionyl*-d-*alanine*, obtained by condensing *d*-alanine with *l*-bromopropionyl chloride in presence of cold sodium hydroxide, melts and decomposes at 165°, and has $[\alpha]_D$ between $-60·4°$ and $-63·6°$. l-*Alanyl*-d-*alanine*, $NH_2\cdot CHMe\cdot CO\cdot NH\cdot CHMe\cdot CO_2H$, prepared by hydrolysing bromopropionylalanine with aqueous ammonia, crystallises in small plates with lancet ends, often in stellate aggregates. It melts at 269—270° (corr.) to a faintly yellow liquid, and has $[\alpha]_D$ $-68·5°$ at 20°. trans-*Alanine anhydride*, obtained by conversion of *l*-alanyl-*d*-alanine into the ester and acting on this with alcoholic ammonia, crystallises in thin, hexagonal, rhombic plates melting at 277—278° (corr.) to a yellow liquid. It is optically inactive and yields an inactive dipeptide on hydrolysis. E. F. A.

Synthesis and Degradation of an Octocyclic Nuclear-homologue of 1 : 4-Dimethylpiperazine Dimethochloride. Ludwig Knorr and Paul Roth (*Ber.*, 1906, **39**, 1420—1429. Compare Abstr., 1904, i, 938; 1905, i, 834).—Dimethyl-γ-chloropropylamine is relatively stable, but on keeping for a month either alone or in aqueous solution it polymerises into *N*-dimethylbistrimethylenediimine dimethochloride. The same change occurs in a day at 100°, and in fifteen hours at 150°. The polymeride is decomposed by a boiling solution of potassium hydroxide, yielding dimethylallylamine, tetramethyltrimethylenediamine, and a *substance*, $C_6H_{10}O$, which is probably *iso*allyl ether, $O(CMe{:}CH_2)_2$.

The following new compounds are described.

Phenyl γ-dimethylaminopropyl ether, $NMe_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot OPh$, obtained by heating an alcoholic solution of phenyl γ-bromopropyl ether

(Lohmann, Abstr., 1891, 1167) and dimethylamine for four hours at 150°, is a colourless oil, which boils at 249—250° under 756 mm. pressure and has a faint ammoniacal odour. The *picrate* melts at 118—119°. When heated with concentrated hydrochloric acid at 170—180°, the substance yields *dimethyl-γ-chloropropylamine hydrochloride*, which crystallises with difficulty and forms an *aurichloride*, $C_5H_{12}NCl,HAuCl_4$, melting at 150°, and a *picrate*,

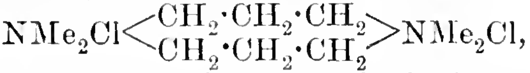
$$C_5H_{12}NCl,C_6H_3O_7N_3,$$

which melts at 110°. The *base*, $CH_2Cl\cdot CH_2\cdot CH_2\cdot NMe_2$, is a colourless oil with a strong ammoniacal odour and boils at 134—135° under 765 mm. pressure. *γ-Dimethylaminopropyl ethyl ether*,

$$NMe_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot OEt,$$

obtained from the base and sodium ethoxide at 150°, is a colourless oil with an ammoniacal odour and boils at 144° under 749 mm. pressure. The *aurichloride*, $C_7H_{17}ON,HAuCl_4$, melts at 70—71°.

N-*Dimethylbistrimethylenedi-imine dimethochloride*,



$$NMe_2Cl{<}{\begin{matrix}CH_2\cdot CH_2\cdot CH_2\\ CH_2\cdot CH_2\cdot CH_2\end{matrix}}{>}NMe_2Cl,$$

is a colourless, hygroscopic substance soluble in water, insoluble in alcohol. The *aurichloride*, $(C_5H_{12}N,AuCl_4)_2$, melts and decomposes at 247—248°. The *platinichloride*, $(C_5H_{12}N)_2PtCl_6$, decomposes at 275—276°.

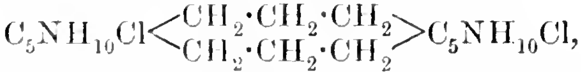
Dimethylallylamine, $C_5H_{11}N$, a decomposition product of the preceding cyclic compound, was also prepared from allyl iodide and an alcoholic solution of dimethylamine at 150°. It boils at 64° under 743 mm. pressure, has a strong ammoniacal odour, dissolves in water, alcohol, or ether, and forms a *picrate* which melts at 95°.

Tetramethyltrimethylenediamine, $NMe_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot NMe_2$, another decomposition product, was also prepared from αγ-dibromopropane and alcoholic dimethylamine at 150°. It boils at 145—146° under 755 mm. pressure and forms a *picrate*, $C_7H_{18}N_2,2C_6H_3O_7N_3$, which sinters and melts at 205°. The *platinichloride*, $C_7H_{18}N_2,H_2PtCl_6$, decomposes at 246—247°. C. S.

Formation of an Octocyclic Polymeride from γ-Chloropropylpiperidine. HEINRICH HÖRLEIN and RUDOLF KNEISEL (*Ber.*, 1906, **39**, 1429—1435. Compare preceding abstract).—1-γ-*Chloropropylpiperidine hydrochloride*, $C_5NH_{10}\cdot C_3H_6Cl,HCl$, obtained by heating 1-γ-phenoxypropylpiperidine (Gabriel and Stelzner, Abstr., 1896, i, 702) and hydrochloric acid at 150° for five hours, crystallises in leaflets, melts at 215—216°, and decomposes at 230°. It can be sublimed in felted, doubly refractive needles. The *base*,

$$C_5NH_{10}\cdot C_3H_6Cl,$$

boils at 210° under 742 mm. pressure. The *aurichloride* melts indefinitely at 100°. When the base is heated in aqueous-alcoholic solution until the liquid has only a faint alkaline reaction, a hygroscopic mass of *bistrimethylenedipiperidinium chloride*,

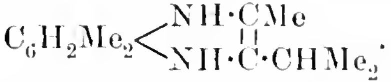


$$C_5NH_{10}Cl{<}{\begin{matrix}CH_2\cdot CH_2\cdot CH_2\\ CH_2\cdot CH_2\cdot CH_2\end{matrix}}{>}C_5NH_{10}Cl,$$

is obtained (compare Gabriel and Stelzner, *loc. cit.*), which is unchanged by hydrochloric acid on the water-bath, is converted by hydrobromic acid into 1-γ-bromopropylpiperidine hydrobromide, and is decomposed by distillation with a 50 per cent. solution of potassium hydroxide into trimethylenedipiperidine (Töhl, Abstr., 1895, i, 681), piperidine, allylpiperidine, and a substance which is probably *iso*allyl ether.

C. S.

A Second 1 : 4-Dihydroquinoxaline. JOHN B EKELEY (*Ber.*, 1906, **39**, 1646—1649. Compare Abstr., 1905, i, 613).—*o*-Xylylene-3 : 5-diamine, obtained by reducing *o*-nitro-*m*-xylidine with zinc dust and sodium hydroxide solution, readily condenses with mesityl oxide in the presence of dry hydrogen chloride, yielding the hydrochloride of 2 : 6 : 8-*trimethyl*-3-iso*propyl*-1 : 4-*dihydroquinoxaline*,



$$C_6H_2Me_2<\begin{matrix}NH\cdot CMe\\ \|\\ NH\cdot C\cdot CHMe_2\end{matrix}.$$

The base crystallises from dilute acetone in brown needles melting at 82—83°, and dissolves readily in organic solvents and in dilute acids. The *hydrochloride*, $C_{14}H_{20}N_2,2HCl$, obtained by passing hydrogen chloride into an ethereal solution of the base, forms a colourless, crystalline precipitate. A yellow *monohydrochloride* also exists. Similar *hydrobromides* and *hydroiodides* have been prepared. When hydrogen chloride is led into a chloroform solution of the base, a colloidal solution of the hydrochloride is obtained. The *picrate*,

$$C_{14}H_{20}N_2,2C_6H_3O_7N_3,$$

forms glistening, yellow needles.

J. J. S.

Quinacridone. FRITZ ULLMANN and RUDOLF MAAG (*Ber.*, 1906, **39**, 1693—1696).—The interaction, for two and a half hours at 140—150°, of anthranilic acid, *p*-dibromobenzene, and potassium carbonate in the presence of amyl alcohol and small quantities of cuprous chloride and copper dust as catalysts leads to the formation of p-*phenylenedianthranilic acid*, $C_6H_4(NH\cdot C_6H_4\cdot CO_2H)_2$, and p-*bromophenylanthranilic acid*, $C_6H_4Br\cdot NH\cdot C_6H_4\cdot CO_2H$; they are separated by means of the weaker basicity of the former acid, which separates from pyridine in lustrous, faintly green leaflets, darkens at 276°, and melts and decomposes at 286°. The latter crystallises in clusters of yellow needles and melts at 182°.

Quinacridone, $C_6H_4<\genfrac{}{}{0pt}{}{NH}{CO}>C_6H_4<\genfrac{}{}{0pt}{}{CO}{NH}>C_6H_4$, obtained by heating *p*-phenylenedianthranilic acid with concentrated sulphuric acid on the water-bath, crystallises in yellow needles, melts at 394°, and dissolves in concentrated sulphuric acid to a yellow solution with a greenish-blue fluorescence.

C. S.

Preparation of *m*-Tolylsemicarbazide. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 162630, 162823, 163035, 163036, 163037, and 163038. Compare Abstr., 1905, i, 383, 949).—*m*-Tolylsemicarbazide may be prepared by the action of carbamic chloride, $NH_2\cdot COCl$, on *m*-tolylhydrazine in benzene solution, the product being washed with water to remove *m*-tolylhydrazine hydrochloride and recrystallised.

Phenyl m-*tolylhydrazinecarboxylate*, $C_6H_4Me\cdot NH\cdot NH\cdot CO_2Ph$, prepared from phenyl chlorocarbonate and *m*-tolylhydrazine, forms colourless crystals and melts at 134°, *methyl* m-*tolylhydrazinecarboxylate* forms white crystals and melts at 119°. Both esters yield *m*-tolylsemicarbazide when warmed with aqueous ammonia.

Benzaldehyde-m-*tolylhydrazone*, $CHPh\cdot CH{:}N\cdot NH\cdot C_6H_4Me$, forms yellowish-white crystals, almost insoluble in water, and melts at 96°. The action of phosgene in benzene solution in the presence of pyridine converts it into the *chloride*, $CHPh\cdot CH{:}N\cdot N(COCl)\cdot C_6H_4Me$, which forms colourless crystals and melts at 69—70°. Alcoholic ammonia reacts with the chloride to form *benzaldehyde*-2-m-*tolylsemicarbazone*, $CHPh\cdot CH{:}N\cdot N(NH_2)\cdot C_6H_4Me$, which separates from water in colourless crystals and melts at 142°. Heating with dilute alcoholic sulphuric acid hydrolyses it to 2-m-*tolylsemicarbazide*, $C_6H_4Me\cdot N(NH_2)\cdot CO\cdot NH_2$, which crystallises in needles and melts at 88°. Heating it to 140° converts it into *m*-tolylsemicarbazide (compare Busch and Walter, Abstr., 1903, i, 522).

m-Tolylhydrazine reacts with cyanogen bromide in ethereal solution, yielding m-*tolylhydrazinonitrile*, $C_6H_4Me\cdot NH\cdot NH\cdot CN$, an easily decomposable oil. Shaking its ethereal solution with dilute hydrochloric acid hydrolyses it to *m*-tolylsemicarbazide. Hydrogen chloride acts on the ethereal solution of the nitrile, giving a white, hygroscopic mass of the *iminochloride*, $C_6H_4Me\cdot NH\cdot NH\cdot CCl{:}NH$. Cyanamide and *m*-tolylhydrazine yield the corresponding *amidine*,

$$C_6H_4Me\cdot NH\cdot NH\cdot C(NH_2){:}NH,$$

crystallising from alcohol in leaflets and melting at 190—192°. Both the iminochloride and the amidine are hydrolysed to *m*-tolylsemicarbazide by bases.

m-Tolylhydrazinonitrile reacts with alcohols and hydrogen haloids in ethereal solution to form *imino-ethers* of *m*-tolylhydrazinecarboxylic acid, $C_6H_4Me\cdot NH{:}NH\cdot C(OR){:}NH\cdot HCl$, which may be hydrolysed to *m*-tolylsemicarbazide. C. H. D.

Methylene-azure. Friedrich Kehrmann and A. Duttenhöfer (*Ber.*, 1906, **39**, 1403—1408).—Methylene-azure, one of the products into which methylene-blue is decomposed by the action either of alkali and air or of silver oxide, has hitherto been regarded as containing oxygen (compare Bernthsen, Abstr., 1886, 53; Fischer and Hepp, Abstr., 1905, i, 948; Hantzsch, this vol., i, 206). The authors show that the two reactions lead to the production of different compounds, which have been isolated and purified in the form of the chlorides. The first reaction gives rise chiefly to *as*-dimethylthionine, the *chloride* of which,  $NH_2\cdot C_6H_3{<}\genfrac{}{}{0pt}{}{-N-}{SCl}{\gg}C_6H_3\cdot NMe_2$, crystallises in brownish-green needles and is identical with the compound synthesised from dimethylaniline and monoaminophenothiazonium chloride. The decomposition of methylene-blue by silver oxide leads to the formation chiefly of trimethylthionine, the *chloride* of which,

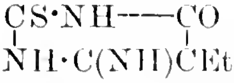
$$NHMe\cdot C_6H_3{<}\genfrac{}{}{0pt}{}{-N-}{SCl}{\gg}C_6H_3\cdot NMe_2,$$

crystallises in metallic-looking green needles very soluble in water, and is identical with the synthetical compound obtained by the thiosulphate method.

Detailed descriptions are given for the purification of the two compounds. C. S.

***CC*-Dialkylbarbituric Acids.** Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 162219. Compare Abstr., 1905, i, 671).—The 4 : 6-dioxy-2-thiodialkylpyrimidines may be oxidised to *CC*-dialkylbarbituric acids by means of nitric or nitrous acids or hydrogen peroxide, the sulphur being thus removed. The compounds employed as starting point for the reaction are prepared by condensing dialkylated ethyl cyanoacetates with thiocarbamide and hydrolysing the iminothiodioxydialkylpyrimidines formed.

Ethyl diethylcyanoacetate condenses with thiocarbamide in presence of sodium ethoxide to form *4-imino-6-oxy-2-thio-5-diethylpyrimidine*,



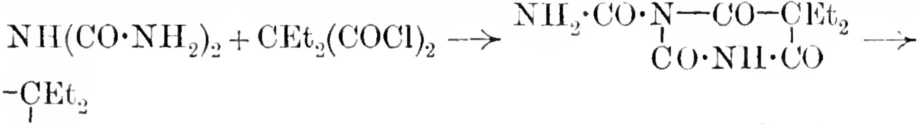
$$\begin{array}{l}\mathrm{CS{\cdot}NH{-}{-}{-}CO}\\ \;|\qquad\qquad\quad |\\ \mathrm{NH{\cdot}C(NH)CEt_2}\end{array}$$

, which crystallises from hot water in yellow needles, melts at 256°, and dissolves readily in dilute alkali hydroxides.

Warming with 30 per cent. sulphuric acid hydrolyses it to 4 : 6-*dioxy-2-thio-5-diethylpyrimidine*, which forms pale yellow needles, melts at 182°, and yields diethylbarbituric acid on oxidation.

4-*Imino-6-oxy-2-thio-5-dimethylpyrimidine* melts at 215° and dissolves sparingly in water or alcohol; 4 : 6-dioxy-2-thio-5-dimethylpyrimidine forms pale yellow needles, melts at 240°, and yields dimethylbarbituric acid on oxidation. C. H. D.

***CC*-Diethylbarbituric Acid.** Emanuel Merck (D.R.-P. 162220. Compare Abstr., 1905, i, 751, and preceding abstract).—Biuret, fused with diethylmalonyl chloride at 130°, forms *CC*-diethylbarbituric acid and cyanuric acid, which may be separated by crystallisation from water:



$$\mathrm{NH(CO{\cdot}NH_2)_2 + CEt_2(COCl)_2} \longrightarrow \begin{array}{l}\mathrm{NH_2{\cdot}CO{\cdot}N{-}CO{-}CEt_2}\\ \qquad\quad\mathrm{CO{\cdot}NH{\cdot}CO}\end{array} \longrightarrow \begin{array}{l}\mathrm{NH{-}CO{-}CEt_2}\\ \mathrm{CO{\cdot}NH{\cdot}CO}\end{array}.$$

C. H. D.

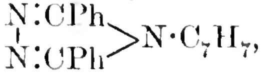
Conversion of Hydrazine Derivatives into Heterocyclic Compounds. XX. Dibenzoylhydrazide Dichloride.

Robert Stollé and Karl Thomä (*J. pr. Chem.*, 1906, [ii], 73, 288—300. Compare preceding abstract).—Dibenzoylhydrazide dichloride,

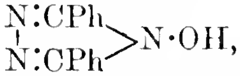
$\mathrm{CClPh{:}N{\cdot}N{:}CClPh}$

(Günther, Abstr., 1889, 1067), is formed together with 2 : 5-diphenyl-1 : 3 : 4-oxadiazole by the action of powdered phosphorus pentachloride on dibenzoylhydrazide at 110°; it crystallises from alcohol in small prisms, melts at 123°, is readily soluble in ether or hot alcohol, does not reduce ammoniacal silver or Fehling's solutions, and is converted into diphenyloxadiazole by boiling with alcoholic silver nitrate or for some time with water. It yields hydrazine hydrochloride when heated with alcoholic hydrogen sulphide at 130° under pressure, 2 : 5-diphenyl-1 : 3 : 4-thiodiazole when heated with phosphorus pentasulphide at 200° in a vacuum, 2 : 5-diphenyl-1 : 3 : 4-triazole and 2 : 5-diphenyl-1 : 3 : 4-oxadiazole when heated with alcoholic ammonia at 180°, and 1 : 2 : 5-triphenyl-1 : 3 : 4-triazole, melting at 292° (m. p. 304—305° : Pellizzari and Alicatore, Abstr., 1901, i, 571), when heated with aniline at 170°.

2 : 5-Diphenyl-1 : 3 : 4-oxadiazole is formed almost quantitatively by the action of phosphorus oxychloride on dibenzoylhydrazide.

2 : 5-*Diphenyl*-1-o-*tolyl*-1 : 3 : 4-*triazole*,  $\begin{matrix}\mathrm{N{:}CPh}\\ | \\ \mathrm{N{:}CPh}\end{matrix}\!>\!\mathrm{N{\cdot}C_7H_7}$, formed by heating dibenzoylhydrazide dichloride with *o*-toluidine at 200°, crystallises from alcohol in small scales and melts at 184° ; the *silver nitrate* derivative crystallises in slender needles and melts and decomposes at 278°.

2 : 5-*Diphenyl*-1-*xylyl*-1 : 3 : 4-*triazole*, $C_{22}H_{19}N_3$, crystallises from alcohol in matted, glistening, slender needles, melts at 252°, and gives a white precipitate with silver nitrate in alcoholic solution.

1-*Hydroxy*-2 : 5-*diphenyl*-1 : 3 : 4-*triazole*,  $\begin{matrix}\mathrm{N{:}CPh}\\ | \\ \mathrm{N{:}CPh}\end{matrix}\!>\!\mathrm{N{\cdot}OH}$, is formed by boiling dibenzoylhydrazide dichloride with hydroxylamine in alcoholic solution in a reflux apparatus. It crystallises from ether in colourless prisms, melts at 185—186°, is soluble in alcohol, ether, benzene, or dilute alkali hydroxides or ammonia, and gives a white precipitate with silver nitrate and ammonia in alcoholic solution.

When heated with hydrazine hydrate in alcoholic solution in a reflux apparatus, dibenzoylhydrazide dichloride yields 3 : 6-diphenyl-1 : 2-dihydro-1 : 2 : 4 : 5-tetrazine.

1-*Benzoyl*-3 : 6-*diphenyl*-1 : 4-*dihydro*-1 : 2 : 4 : 5-*tetrazine*,

$$\mathrm{CPh}\!<\!\begin{matrix}\mathrm{N{\cdot}NBz}\\ \mathrm{NH{-}N}\end{matrix}\!>\!\mathrm{CPh},$$

is formed together with dibenzoylhydrazide by heating dibenzoylhydrazide dichloride with benzoyl hydrazide at 130—135° ; it separates from alcohol in transparent crystals, melts at 240°, dissolves in alcohol, dilute alkali hydroxides, or ammonia, forms a precipitate with silver nitrate and a small quantity of ammonia, and is hydrolysed by alcoholic-aqueous hydrogen chloride at 130—140° under pressure, forming 3 : 6-diphenyl-1 : 4-dihydro-1 : 2 : 4 : 5-tetrazine.

1-*Benzoyl*-3 : 6-*diphenyl*-1 : 2-*dihydro*-1 : 2 : 4 : 5-*tetrazine*,

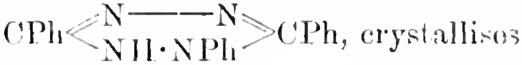
$$\mathrm{CPh}\!<\!\begin{matrix}\mathrm{N{-\!\!-\!\!-}N}\\ \mathrm{NH{\cdot}NBz}\end{matrix}\!>\!\mathrm{CPh},$$

is formed by boiling 3 : 6-diphenyl-1 : 2-dihydro-1 : 2 : 4 : 5-tetrazine with benzoyl chloride in benzene in presence of sodium carbonate in a reflux apparatus. It crystallises from benzene in lemon-yellow needles, melts and decomposes at 208°, and does not reduce Fehling's or ammoniacal silver solutions.

1 : 3 : 6-*Triphenyl*-1 : 4-*dihydro*-1 : 2 : 4 : 5-*tetrazine*,

$$\mathrm{CPh}\!<\!\begin{matrix}\mathrm{NH{-}N}\\ \mathrm{N{\cdot}NPh}\end{matrix}\!>\!\mathrm{CPh},$$

is formed, together with the hydrochloride of the 1 : 2-dihydro-base, by heating dibenzoylhydrazide dichloride with phenylhydrazine in alcoholic solution in a reflux apparatus ; it is colourless, melts at 263°, is only slightly soluble in alcohol or dilute acids, reduces Fehling's solution on prolonged boiling, gives a white precipitate with silver nitrate and ammonia in alcoholic solution, and is converted by nitrous acid into 2 ; 5-diphenyl-1 : 3 : 4-triazole.

1 : 3 : 6-*Triphenyl*-1 : 2-*dihydro*-1 : 2 : 4 : 5-*tetrazine hydrochloride* melts at 180°, is readily soluble in water, and is hydrolytically dissociated when boiled with water. The *base*,  $\mathrm{CPh}{<}\begin{matrix}\mathrm{N{-}{-}{-}N}\\ \mathrm{NH\cdot NPh}\end{matrix}{>}\mathrm{CPh}$, crystallises from alcohol in glistening, golden, slender needles, melts at 126°, and is readily soluble in the ordinary organic solvents. It yields hydrazine when boiled with dilute hydrochloric acid, reduces alcoholic silver nitrate, is converted into diphenyloxadiazole when treated with nitrous acid, and changes into the *s*-isomeride when boiled with alcoholic hydrogen chloride.

Dibenzoylhydrazide diethyl ether, $\mathrm{OEt\cdot CPh{:}N\cdot N{:}CPh\cdot OEt}$, formed together with 2 : 5-diphenyloxadiazole by boiling the dichloride with sodium ethoxide in alcoholic solution in a reflux apparatus, crystallises in colourless octahedra and melts at 83—84°. G. Y.

Condensation Products of *N*-Substituted *o*-Diamines with Alloxan and its Derivatives. OTTO KÜHLING and O. KASELITZ (*Ber.*, 1906, 39, 1314—1326. Compare Abstr., 1893, i, 324).—*Alloxanylphenyl*-o-*phenylenediamine*,

$$\mathrm{NHPh\cdot C_6H_4\cdot N{:}C}{<}\begin{matrix}\mathrm{CO\cdot NH}\\ \mathrm{CO\cdot NH}\end{matrix}{>}\mathrm{CO},$$

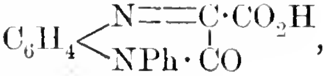
prepared from phenyl-*o*-phenylenediamine and alloxan, separates from glacial acetic acid in yellow crystals and melts at 232°. Its solution in concentrated sulphuric acid is cherry-red; its solution in hydrochloric or nitric acid is reddish-yellow.

Anilinophenyliminoalloxanic acid,

$$\mathrm{NHPh\cdot C_6H_4\cdot N{:}C(CO_2H)\cdot CO\cdot NH\cdot CO\cdot NH_2},$$

prepared by the action of dilute sodium hydroxide on the preceding compound, separates from a mixture of acetone and light petroleum in tetragonal leaflets and melts at 228°.

2-*Keto*-1-*phenyl*-1 : 2-*dihydroquinoxaline*-3-*carboxylic acid*,

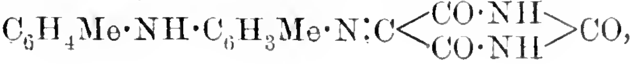


$$\mathrm{C_6H_4}{<}\begin{matrix}\mathrm{N{=\!=}C\cdot CO_2H}\\ \mathrm{NPh\cdot CO}\end{matrix},$$

prepared by boiling alloxanylphenyl-*o*-phenylenediamine with an excess of sodium carbonate, separates from dilute alcohol in leaflets and melts at 177°. It forms a reddish-yellow solution with concentrated sulphuric acid, and a yellow solution with hydrochloric or with nitric acid. Its *barium* salt forms yellow needles.

2-*Keto*-1-*phenyl*-1 : 2-*dihydroquinoxaline*,  $\mathrm{C_6H_4}{<}\begin{matrix}\mathrm{N{=\!=}CH}\\ \mathrm{NPh\cdot CO}\end{matrix}$, prepared by heating the preceding acid above its melting point until the evolution of carbon dioxide ceases, separates from dilute alcohol in bright yellow needles and melts at 167°. Its solution in concentrated sulphuric acid is green, and on dilution becomes red and then yellow; its solution in hydrochloric or nitric acid is yellowish-red.

Alloxanyl-o-*amino-di*-p-*tolylamine*,



$$\mathrm{C_6H_4Me\cdot NH\cdot C_6H_3Me\cdot N{:}C}{<}\begin{matrix}\mathrm{CO\cdot NH}\\ \mathrm{CO\cdot NH}\end{matrix}{>}\mathrm{CO},$$

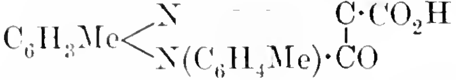
prepared from alloxan and *o*-amino-di-*p*-tolylamine, separates from glacial acetic acid in yellow needles and melts at 244°. Its solution in sulphuric acid is cherry-red; its solution in hydrochloric or nitric acid is reddish-yellow.

p-*Toluidino*-m-*tolyliminoalloxanic acid*,

$$C_6H_4Me\cdot NH\cdot C_6H_3Me\cdot N\colon C(CO_2H)\cdot CO\cdot NH\cdot CO\cdot NH_2,$$

prepared by the action of cold dilute sodium hydroxide on the preceding compound, melts at 240°.

2-*Keto*-1-p-*tolyl*-6-*methyl*-1 : 2-*dihydroquinoxaline*-3-*carboxylic acid*,



$C_6H_3Me<\begin{array}{l}N\text{———}\overset{}{C}\cdot CO_2H\\ N(C_6H_4Me)\cdot CO\end{array}$, prepared by boiling alloxanyl-*o*-amino-di-*p*-tolylamine with sodium carbonate, separates from dilute alcohol in hexagonal leaflets and melts at 194°. It forms a reddish-yellow solution with concentrated sulphuric acid and a yellow solution with hydrochloric or nitric acid. Its *barium* salt ($+4\frac{1}{2}H_2O$) and *zinc* salt ($+2H_2O$) are described.

2-*Keto*-1-p-*tolyl*-6-*methyl*-1 : 2-*dihydroquinoxaline*,

$$C_6H_3Me<\begin{array}{l}N\text{=======}CH\\ N(C_6H_4Me)\cdot CO\end{array},$$

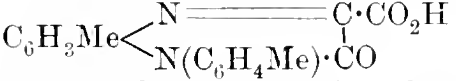
prepared by heating the preceding acid above its melting point, forms yellow needles and melts at 170—171°. Its solution in sulphuric acid is brown, and on dilution becomes red and then yellow.

p-*Toluidino*-p-*tolyliminoalloxanic acid*,

$$C_6H_3Me\cdot NH\cdot C_6H_3Me\cdot N\colon C(CO_2H)\cdot CO\cdot NH\cdot CO\cdot NH_2,$$

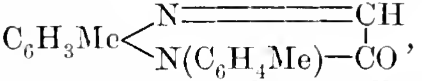
prepared by shaking alloxanyl-*o*-amino-*m*-tolyl-*p*-tolylamine with dilute sodium hydroxide, crystallises in leaflets and partially melts at 180°, solidifies, and melts again at 248°.

2-*Keto*-1-p-*tolyl*-7-*methyl*-1 : 2-*dihydroquinoxaline*-3-*carboxylic acid*,



$C_6H_3Me<\begin{array}{l}N\text{=======}C\cdot CO_2H\\ N(C_6H_4Me)\cdot CO\end{array}$, crystallises from dilute alcohol in tetragonal leaflets and melts at 193°. Its *barium* salt ($+1\frac{1}{2}H_2O$) forms yellow needles.

2-*Keto*-1-p-*tolyl*-7-*methyl*-1 : 2-*dihydroquinoxaline*,



$$C_6H_3Me<\begin{array}{l}N\text{=======}CH\\ N(C_6H_4Me)\text{—}CO\end{array},$$

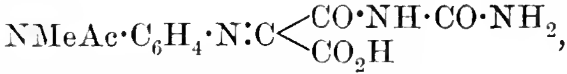
separates from dilute alcohol in yellow needles and melts at 173°. Its solution in sulphuric acid is brown, and becomes red and then yellow on dilution. Its solution in hydrochloric or nitric acid is yellow.

Alloxanylmethyl-o-*phenylenediamine*,

$$NHMe\cdot C_6H_4\cdot N\colon C<\begin{array}{l}CO\cdot NH\\ CO\cdot NH\end{array}>CO,$$

prepared from alloxan and *N*-methyl-*o*-phenylenediamine, separates from glacial acetic acid in yellow needles and melts at 224°. Its solution in sulphuric acid is cherry-red, and in hydrochloric or nitric acid yellowish-red.

The *acetyl* derivative,



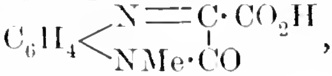
$NMeAc\cdot C_6H_4\cdot N\colon C<\begin{array}{l}CO\cdot NH\cdot CO\cdot NH_2\\ CO_2H\end{array}$, crystallises in needles and melts and decomposes at 265—270°.

Methylaminophenyliminoalloxanic acid,

$$NHMe{\cdot}C_6H_4{\cdot}N{:}C(CO_2H){\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2,$$

prepared by the action of sodium carbonate on alloxanylmethyl-*o*-phenylenediamine, separates from a mixture of acetone and light petroleum in needles and melts at 224°. Its solutions in concentrated mineral acids are red.

2-*Keto*-1-*methyl*-1 : 2-*dihydroquinoxaline*-3-*carboxylic acid*,

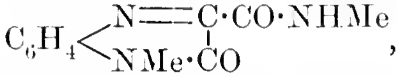


$$C_6H_4{<}\begin{array}{l}N{=\!=}C{\cdot}CO_2H\\ NMe{\cdot}CO\end{array},$$

prepared by boiling alloxanylmethyl-*o*-phenylenediamine with sodium carbonate until the evolution of ammonia ceases, forms yellow needles and melts at 174°. Its solution in sulphuric acid is reddish-yellow, and in hydrochloric or nitric acid yellow. Its *barium* salt $(+1\frac{1}{2}H_2O)$ forms needles.

2-*Keto*-1-*methyl*-1 : 2-*dihydroquinoxaline*,  $C_6H_4{<}\begin{array}{l}N{=\!=}CH\\ NMe{\cdot}CO\end{array}$, separates from dilute acetone in yellowish-white needles and melts at 122°. It forms a yellowish-green solution with sulphuric acid and a yellow solution with hydrochloric or nitric acid.

2-*Keto*-1-*methyl*-1 : 2-*dihydroquinoxaline*-3-*methylamide*,



$$C_6H_4{<}\begin{array}{l}N{=\!=}C{\cdot}CO{\cdot}NHMe\\ NMe{\cdot}CO\end{array},$$

prepared from methyl-*o*-phenylenediamine and methylalloxan, crystallises from dilute alcohol in yellow needles and melts at 166°. Its solution in sulphuric acid is cherry-red. When boiled with potassium or sodium hydroxide, it forms 2-keto-1-methyl-1 : 2-dihydroquinoxaline-3-carboxylic acid. A. McK.

Tetrazoline. Reply to R. Stollé. SIEGFRIED RUHEMANN (*Ber.*, 1906, **39**, 1228—1231).—Dimethyltetrazoline,  $CMe{<}\begin{array}{l}N{\cdot}NH\\ NH{\cdot}N\end{array}{>}CMe$, yields with methyl iodide a colourless *iodide*, $C_5H_{11}N_4I$, from which a brown *periodide*, $C_5H_{11}N_4I_3$, can be obtained. Alkaline solutions of this periodide do not become violet on exposure to air.

The original formula for benzylidenetetrazoline (Ruhemann and Merriman, Trans., 1905, **87**, 1768) is retained, and it is suggested that the products obtained from *s*-diphenyltetrazoline and aldehydes may be differently constituted (compare Stollé, this vol., i, 315). J. J. S.

Behaviour of Certain Azo-compounds towards Hydrogen Chloride. MAX BUSCH and HERMANN BRANDT (*Ber.*, 1906, **39**, 1395—1400).—Benzeneazoanilinophenyliminomethane,

$$N_2Ph{\cdot}C(N{\cdot}Ph){\cdot}NHPh,$$

is dissolved by alcoholic hydrogen chloride to a colourless solution, from which the *hydrochloride* of *p*-chloroanilinodiphenylguanidine, $C_6H_4Cl{\cdot}NH{\cdot}NH{\cdot}C(NPh){\cdot}NHPh$, can be obtained. A second, but not a third, halogen atom can be introduced in a similar way into an *ortho*-position in the same nucleus (compare Marckwald and Wolff, Abstr., 1893, i, 25 ; Hantzsch and Singer, *ibid.*, 1897, i, 216 ; Jacobsen, *Chem. Centr.*, 1898, ii, 36 ; Bamberger, Abstr., 1902, i, 246).

p-*Chloroanilinodiphenylguanidine* crystallises in pale red prisms and melts at 154°. The *hydrochloride*, $C_{19}H_{17}N_4Cl,HCl$, forms clusters of colourless prisms and melts at 216°. The base in boiling alcoholic solution is converted by mercuric oxide into p-*chlorobenzeneazoanilinophenyliminomethane*, $C_6H_4Cl\cdot N_2\cdot C(NPh)\cdot NHPh$, which crystallises in blood-red, glistening needles and melts at 155°. 2:4-*Dichloroanilinodiphenylguanidine hydrochloride*,

$$C_6H_3Cl_2\cdot NH\cdot NH\cdot C(NPh)\cdot NHPh,HCl,$$

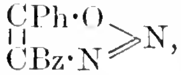
obtained from the preceding compound and alcoholic hydrogen chloride at 40—50°, crystallises in obliquely truncated, flattened prisms, darkens at 225°, and melts and decomposes at 242°. The *base*, $C_{19}H_{16}N_4Cl_2$, crystallises in colourless prisms and melts at 125°. 2:4-*Dichlorobenzeneazoanilinophenyliminomethane*,

$$C_6H_3Cl_2\cdot N_2\cdot C(NPh)\cdot NHPh,$$

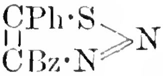
crystallises in small, brownish-red needles and melts at 130°. Cold alcoholic hydrogen chloride dissolves it, forming a reddish-brown solution, from which the hydrochlorides of aniline and of dichloroanilinodiphenylguanidine are obtained, but not a trichloro-derivative.

C. S.

Diazotation of Dibenzoylmethane. HEINRICH WIELAND and SIEGFRIED BLOCH (*Ber.*, 1906, **39**, 1488—1491. Compare Abstr., 1904, i, 596, 656).—Dibenzoyldiazomethane has the constitution of a diazoanhydride,



$\left.\begin{matrix}\mathrm{CPh\cdot O}\\ \|\\ \mathrm{CBz\cdot N}\end{matrix}\right>N$, as when treated with ammonium and hydrogen sulphides in alcoholic solution it yields 4-*benzoyl*-5-*phenyl*-1:2:3-*thiodiazole*,



$\left.\begin{matrix}\mathrm{CPh\cdot S}\\ \|\\ \mathrm{CBz\cdot N}\end{matrix}\right>N$, which crystallises in glistening, colourless scales, melts at 90—91°, and becomes violet, and finally yellow on exposure to light.

Anilinodibenzoylmethane forms a yellow, crystalline *nitrosoamine*, $CHBz_2\cdot NPh\cdot NO$, which melts and decomposes at 92° and gives Liebermann's reaction.

G. Y.

Azo-dye from *m*-Aminobenzeneazo-*m*-toluidine. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 162627).—Diazotised *m*-aminobenzeneazo-*m*-toluidine combines with β-naphthol to form an insoluble bordeaux-red azo-dye, which may be bleached white in printing by means of the formaldehyde-hyposulphite compound.

C. H. D

Equilibrium between Proteids and Electrolytes. II. Precipitation of Egg-albumin with Sodium Sulphate. G. GUERRINI (*Zeit. physiol. Chem.*, 1906, **47**, 287—293. Compare Galeotti, *ibid.*, 1904, **40**, 5).—The precipitation of egg-albumin by means of sodium sulphate depends on the concentration of the sulphate solution, and the solid phase obtained consists of egg-albumin only. This is proved by showing that the precipitate contains only an amount of sulphate corresponding with what should be present in the amount of solution of known concentration absorbed by the precipitate.

A simple method is described for estimating the amounts of water, albumin, and sodium sulphate in a solution.

It is shown that in the three-component system containing the phases $Na_2SO_4,10H_2O$ solid, albumin (solid), solution, the concentration of the solution can vary considerably even when the temperature is constant. There appears, however, to be a regularity between the variations in the concentration of the albumin and of the sulphate.

This exception to the phase rule may be due to the fact that one of the substances is a colloid. J. J. S.

Precipitation of Egg-albumin by other Colloids and its Relationship to the Reactions of Immune Substances. Ulrich Friedemann (*Arch. Hygiene*, 1906, **55**, 361—389. Compare Abstr., 1904, ii, 546).—Serum and egg-albumin are precipitated by inorganic colloids, such as metals, sulphides, acid oxides, or basic oxides, irrespective of whether these are electro-positive or electro-negative in character. The influence of the addition of salts is partly accelerating and partly retarding, the net result depending on the relative proportions of colloid and albumin in the mixture. The sign of the electric potential of the albumin compared with water does not control its precipitation by inorganic colloids, inasmuch as Hardy's coagulated egg-albumin, which wanders to the anode, gives copious precipitates with every colloid investigated. The precipitating power of ions is a function of their dielectric attraction on the water. The *rôle* of salts in precipitin reactions is very similar to that in colloid albumin precipitations, an amphoteric colloid probably reacting with an acid or a basic colloid. Bacteria can be agglutinated by a salt-free serum even in such dilutions as 1 : 1000. In this respect, normal and immune sera behave alike. E. F. A.

Compounds of Catechol Monoalkyl Ethers with Proteids. H. C. Fehrlin (D.R.-P. 162656).—When guaiacol, either fused or dissolved in alcohol, is stirred into an aqueous solution of egg-albumin, the whole soon solidifies to a paste. The product is collected, drained, dried under reduced pressure, and heated at 115—120°, when it becomes insoluble in gastric juice. After washing with toluene and again drying, it forms a light brown powder, containing 25 per cent. of guaiacol, insoluble in ordinary solvents, but soluble in cold dilute alkali hydroxides.

Similar products are obtained from other monoalkyl ethers of catechol, and from other proteids, albumoses, and peptones. The compounds find therapeutic application. C. H. D.

Polymerisation of Globulins. Alonzo E. Taylor (*J. Biol. Chem.*, 1906, **1**, 345—354).—Euglobulin and pseudo-globulin prepared from serum, when dry, remain unchanged for years. In presence of distilled water, each is partly transformed into the other. This is a reversible action, and is attributed to polymerisation. As in other instances quoted, there is a tendency to equilibrium in the system, and the law of mass action holds. Viewed as a chemical transformation, three possibilities are discussed: (1) condensation, (2) union with water. and (3) intramolecular rearrangement. The transformation of albumin into globulin is believed to come into the same category. Further, it was found that the globulins in distilled water, and especially the pseudo-globulins, are in part auto-hydrolysed with the formation of proteoses. W. D. H.

Hæmatogen and the Formation of Hæmoglobin. Louis Hugounenq and Albert Morel (*Compt. rend.*, 1906, **142**, 805—806. Compare Abstr., 1905, ii, 566; 1906, ii, 95).—Hæmatogen, the parent substance of hæmoglobin in egg-yolk, yields a proteid residue, which, like globin and other histones, is rich in diamino-nitrogen. It also yields on hydrolysis a black pigment (C, 65·9; H, 4·37; N, 6·67, and Fe, 2·6 per cent.) which is regarded as analogous to hæmatin, and named *hæmatovin.* It is possible that hæmatovin may be an intermediate stage in hæmatin formation during life. In chlorosis, Seiller and Freund have found in the blood an uncoloured nucleo-proteid containing iron. It is possible the presence of such a substance may account for discrepancies between estimations of iron and of hæmoglobin in the blood. W. D. H.

Bile Pigments. William Küster (*Zeit. physiol. Chem.*, 1906, **47**, 294—326).—By working with powdered gall stones, the use of hydrochloric acid can be avoided, and 10 per cent. acetic acid employed instead. Hot glacial acetic acid extracts a hitherto undescribed green pigment, *choleprasin*; it is insoluble in alcohol. β-Bilirubin is easily soluble in chloroform and is an artificial product which contains chlorine; from it the chlorine is easily separable. Most impure bilirubins obtained by chloroform contain chlorine. From pure bilirubin by the action of chloroform in the dark, a green pigment soluble in glacial acetic acid is formed in small quantities. On keeping, bilirubin undergoes a change, probably a polymerisation. This modification passes by recrystallisation from dimethylaniline into the form soluble in chloroform. Bilirubin crystallises from hot dimethylaniline in broad rhombic plates or from chloroform in long needles.

W. D. H.

The Carbohydrate Group of the Nucleo-proteid of the Spleen. I. Phoebus A. Levene and John A. Mandel (*Zeit. physiol. Chem.*, 1906, **47**, 151—153).—The carbohydrate group in nucleo-proteid is usually a pentose (xylose). The nucleo-proteid of the spleen after suitable treatment gave the orcinol reaction for pentose, and reduced Fehling's solution after preliminary treatment with hydrochloric acid. Glucothionic acid was also separated, but it is not clear whether this came from the nucleo-proteid or from mucoid mixed with it. W. D. H.

Nucleic Acids. XII. Nucleic Acid of the Kidney. John A. Mandel and Phoebus A. Levene (*Zeit. physiol. Chem.*, 1906, **47**, 140—142. Compare this vol., i, 125).—The occurrence of nucleo-proteid in the kidney has been described by Halliburton and by Lönnberg, but its products of decomposition have not been investigated.

In the present research, the nucleic acid separated from the nucleoproteid contained 6·25 per cent. of phosphorus, and yielded, on decomposition with acid, guanine, adenine, thymine, cytosine, and lævulic acid. One hundred grams of substance yielded adenine picrate 2·20, guanine 7·32, thymine 3·6, and cytosine picrate 12·24 grams. The nucleic acid gave the typical pentose reaction with orcinol hydrochloride. W. D. H.

Jecorin. Richard Waldvogel and Tintemann (*Zeit. physiol. Chem.*, 1906, **47**, 129—139).—Jecorin obtained from autolysed livers and spleen contains from 8 to 9·8 per cent. of nitrogen and from 2 to 3·4 per cent. of phosphorus. These numbers are very different from those obtained by other observers; for instance, Drechsel gives the percentage of nitrogen as 4·36, Baldi as 2·14, and Manasse as 0·3. The authors, nevertheless, regard it as a chemical individual, derived from lecithin. Some preparations reduced Fehling's solution, some did not.

W. D. H.

Decomposition of Gelatin. Phoebus A. Levene and George B. Wallace (*Zeit. physiol. Chem.*, 1906, **47**, 143—148. Compare Abstr., 1903, i, 301; 1904, i, 357).—On tryptic digestion of gelatin, the pyrrolidine-2-carboxylic acid formed is identical with the optically inactive pyrrolidine-2-carboxylic acid. After fifteen months' digestion of 1500 grams of gelatin with trypsin, the mixture was neutralised, evaporated to a syrupy consistency, taken up in 5 per cent. sulphuric acid, and fractionally precipitated with phosphotungstic acid. From the first precipitate, a substance was separated of the formula $C_7H_{10}O_2N_2$; further work on this is in progress. From the fourth precipitate, glycine was separated. The other precipitates are not yet examined. W. D. H.

Swelling of Gelatin in Salt Solutions. Wolfgang Ostwald (*Pflüger's Archiv*, 1906, **111**, 581—606. Compare Abstr., 1905, i, 845, 954).—In regard to the influence of salts on the swelling of gelatin, the influence of concentration of acids, alkalis, chlorides, and nitrates was found to be of a specific nature, and the curves show no parallelism to a single factor (such as osmotic pressure), but present several maxima and minima. The first part of such curves indicates adsorption is occurring for reasons which are explained in full. There is further a parallelism between the curve of swelling and that of viscosity.

W. D. H.

Action of the Rennet Ferment on Casein. Eugen Petry (*Chem. Centr.*, 1906, i, 1032; from *Wien. Klin. Woch.*, **19**, 143—144).—The action of rennet on casein free from calcium does not cease with the formation of paracasein. The nature of the action as regards products is similar to that of ordinary proteolytic ferments. Primary albumoses (caseose) are formed, as well as a modification of paracasein which is not precipitated by lime, by heating, or by dilute zinc sulphate.

Rennet extract (Merck) is without action on serum albumin, boiled egg-albumin, and gelatin. N. H. J. M.

Influence of Peroxydase on Alcoholic Fermentation. Alexis Bach (*Ber.*, 1906, **39**, 1664—1668).—An aqueous solution of sucrose was acted on by a mixture of peroxydase (prepared as in former experiments by the author) and hydrogen peroxide in the presence of the solid precipitated from yeast juice by the addition of acetone ("Aceton-Dauerhefe"). The effect of the peroxydase as estimated by the volume of carbon dioxide produced was thus studied. The whole of the hydrogen peroxide present was decomposed with the evolution of oxygen. The presence of the active peroxydase has a strong inhibiting action on alcoholic fermentation in the cases studied. When the peroxydase is first boiled and then added to the solution containing sucrose, &c., the presence of the hydrogen peroxide has no inhibiting effect; hydrogen peroxide in the absence of peroxydase also has no inhibiting effect. The presence of peroxydase and of hydrogen peroxide has no effect on the acidity of the liquid after fermentation.

The capability which the solid precipitated from yeast juice by acetone possesses of liberating oxygen from hydrogen peroxide is diminished by the presence of active peroxydase. A. McK.

Fate of Yeast Catalase in Cell-free Alcoholic Fermentation. Alexis Bach (*Ber.*, 1906, **39**, 1669—1670. Compare preceding abstract).—The author has examined the diminution in the amount of catalase of precipitated yeast juice during alcoholic fermentation and draws the conclusions: (1) that the amount of catalase in precipitated yeast juice decreases regularly, although slowly, during autolysis, (2) that, in the presence of sucrose, the destruction of the catalase is very much quicker than during autolysis, and (3) that the destruction of the catalase increases in both cases with diminution of the concentration of the precipitated yeast juice. A. McK.

Influence of Peroxydase on the Activity of Catalase. Alexis Bach (*Ber.*, 1906, **39**, 1670—1672. Compare preceding abstracts).—Yeast catalase did not diminish in activity on prolonged contact with active peroxydase at 30°. A. McK.

Alcoholic Ferment of Yeast Juice. Arthur Harden and William J. Young (*Proc. Roy. Soc.*, 1906, **77**, *B*, 405—420. Compare *Proc.*, 1905, **21**, 189; Abstr., 1905, ii, 109; also Buchner and Antoni, this vol., i, 56).—The total fermentation produced by yeast juice acting on excess of dextrose is, as a rule, doubled by the addition of an equal volume of boiled and filtered juice, and further increased by a greater volume, the sugar concentration being kept constant. The constituent of the juice to which this effect is due is removed when the liquid is dialysed in a parchment tube, leaving an inactive residue. It is possible by filtering the juice through a Martin gelatin filter to divide the yeast-juice into an inactive residue and a dialysate which, although itself inert, is capable of rendering this residue active.

Two phenomena are concerned in the production of the increased fermentation in the presence of boiled yeast juice: (*a*) an initial rapid evolution of carbon dioxide is produced which soon diminishes until a rate is attained which remains nearly constant for several hours; (*b*) the fermentation rate diminishes more slowly, so that fermentation continues for a longer period. To the latter the greater proportion of the total increase is due.

The extra quantity of carbon dioxide evolved in the initial period is directly proportional to the volume of boiled juice added. A similar initial rapid evolution of gas is produced on the addition of soluble phosphates, the increase corresponding exactly with the amount of phosphate added. A second rapid evolution of carbon dioxide sets in on adding a second quantity of phosphate after a steady rate is attained subsequent to the first addition. Fermentation in the presence of phosphates is a normal alcoholic fermentation, the ratio of alcohol to carbon dioxide being 1·13. The soluble phosphate is converted into a non-precipitable form by the reaction, possibly into a phosphoric ester of dextrose. E. F. A.

Mercurinitrophenols. ARTHUR HANTZSCH and SAMUEL M. AULD (*Ber.*, 1906, **39**, 1105—1117).—Two types of nitrophenol derivatives containing mercury have been obtained, the true mercuric nitrophenoxides exhibiting in solution the reactions of mercury ions, and mercurinitrophenols in which the atom of mercury is attached to the benzene nucleus. The latter compounds usually resemble the nitrophenols in chemical behaviour and absorption of light, and are therefore regarded as solid solutions of the *aci*-form in the true colourless mercurinitrophenols, $HO{\cdot}C_6H_3{<}\begin{matrix}NO_2\\HgX\end{matrix} \rightleftarrows O{:}C_6H_5{<}\begin{matrix}NO{\cdot}OH\\HgX\end{matrix}$. From the mercuric nitrophenoxides, intensely-coloured anhydrides are obtained to which formulæ such as $O{:}C_6H_3{<}\begin{matrix}NO\\Hg\end{matrix}{>}O$ are ascribed.

Mercuripicric anhydride, $O{:}C_6H(NO_2)_2{<}\begin{matrix}NO\\Hg\end{matrix}{>}O$, is obtained by boiling for several hours freshly-precipitated mercuric oxide with an aqueous solution of picric acid. It forms small, pale yellow crystals, decomposes without melting, is a non-electrolyte in aqueous solution, and does not show the reactions of mercuric ions. Dilute hydrochloric acid converts it into *mercurichloride-trinitrophenol*, $OH{\cdot}C_6H(NO_2)_3{\cdot}HgCl$, which separates from chloroform in small crystals with a faint yellow colour and melts at 118°. When treated with sodium hydroxide, it yields *sodium mercurihydroxide-picrate*, $O{:}C_6H(NO_2)_2(NO{\cdot}ONa){\cdot}Hg{\cdot}OH$, which separates from alcohol in yellow needles and decomposes by rapid heating. *Mercurihydroxide-picric acid*, $OH{\cdot}C_6H(NO_2)_3{\cdot}Hg{\cdot}OH$, results by the action of dilute sulphuric acid on the preceding compound or directly on the anhydride, and is obtained colourless from alcohol or acetone.

Mercuri-aci-2 : 4-*dinitrophenol anhydride*, $O{:}C_6H_2(NO_2){<}\begin{matrix}NO\\Hg\end{matrix}{>}O$, is obtained by boiling freshly-precipitated mercuric oxide for sixteen hours with an aqueous solution of the calculated quantity of dinitrophenol. It is obtained pure as a pale yellow powder by heating its *compound* with pyridine, $C_6H_2O_5N_2Hg,C_5NH_5$, and in aqueous solution does not yield mercury ions. The replacement of mercury by bromine leads to the formation of *o*-bromodinitrophenol. *Mercurichloride-dinitrophenol*, $OH{\cdot}C_6H_2(NO_2){\cdot}HgCl$, obtained from the anhydride and dilute hydrochloric acid, is a colourless crystalline powder and melts and blackens at 182°; by the Schotten-Baumann reaction, a colourless benzoyl derivative is obtained.

Sodium mercurihydroxide-aci-*dinitrophenoxide*,

$$O{:}C_6H_2(NO_2)(NO{\cdot}ONa){\cdot}Hg{\cdot}OH,$$

obtained from the chloride by the action of concentrated sodium hydroxide, separates from water or dilute alcohol in orange-red prisms containing $1H_2O$ and explodes when strongly heated. Dilute sulphuric acid converts it into *mercurihydroxide-dinitrophenol*,

$$OH{\cdot}C_6H_2(NO_2)_2{\cdot}Hg{\cdot}OH,$$

which separates from alcohol as a colourless, microcrystalline powder.

Mercuri-aci-p-*nitrophenol anhydride*, $O{:}C_6H_3{<}\begin{smallmatrix}NO\\Hg\end{smallmatrix}{>}O$, is a yellow powder obtained by the prolonged boiling of a dilute alcoholic solution of mercuric acetate and sodium *p*-nitrophenoxide. The *pyridine* compound, $C_6H_3O_3NHg,C_5NH_5$, is a scarlet powder and decomposes at 190° into its constituents. The mercury must be ortho to the hydroxyl group, since 2 : 6-dibromo-*p*-nitrophenol does not yield a corresponding derivative.

Mercurichloride-p-*nitrophenol*, $OH{\cdot}C_6H_3(NO_2){\cdot}HgCl$, is colourless and melts at 175°. *Sodium mercurihydroxide*-aci-p-*nitrophenoxide*, $O{:}C_6H_3(NO{\cdot}ONa){\cdot}Hg{\cdot}OH$, crystallises with $\frac{1}{2}H_2O$ and darkens and decomposes on heating.

Mercurihydroxide-p-*nitrophenol* separates from boiling alcohol as an amorphous powder and melts at 206°; its solutions in acetone, alcohol, or acetic acid are colourless, in pyridine faintly yellow.

Mercuri-aci-o-*nitrophenol anhydride*, $O{:}C_6H_3{<}\begin{smallmatrix}Hg\\NO\end{smallmatrix}{>}O$, is a yellow powder and by treatment with bromine yields *p*-bromo-*o*-nitrophenol. *Mercurichloride*-o-*nitrophenol*, $OH{\cdot}C_6H_3(NO_2){\cdot}HgCl$, forms colourless solutions in acetic acid or acetone, but dissolves in pyridine with a yellow colour. *Sodium mercurihydroxide*-o-*nitrophenoxide* separates from dilute alcohol in dark red crystals. *Mercurihydroxide*-o-*nitrophenol* forms pale yellow crystals and melts and decomposes at 240—250°.

C. S.

Organic Chemistry.

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isoHexane and a New Dodecane. Latham Clarke and R. Norris Shreve (*Amer. Chem. J.*, 1906, **35**, 513—519).—*iso*Hexane (ethyl*iso*butyl) can be prepared in a yield of 57 per cent. of the theoretical by the reduction of methyl*iso*butylcarbinol. Methyl *iso*butyl ketone, prepared by boiling ethyl *iso*propylacetoacetate for six hours with 10 per cent. potassium hydroxide, boils at 119° under 765 mm. pressure. Methyl*iso*butylcarbinol can be obtained by mixing an ethereal solution of the ketone with water and gradually adding sodium; a small quantity of *methylisobutylpinacone*,

$$CH_2Pr^{\beta}\cdot CMe(OH)\cdot CMe(OH)\cdot CH_2Pr^{\beta},$$

is produced simultaneously as a viscous, oily liquid which has a fishy odour, boils at 245°, and is soluble in alcohol, ether, ethyl acetate, acetone, benzene, or glacial acetic acid, and insoluble in water. On reducing this pinacone with hydrogen iodide, *methyl*iso*butylcarbinyl iodide*, $CHMe_2\cdot CH_2\cdot CHMeI$, is obtained as a colourless, oily liquid which boils and partially decomposes at 158—160°, and is soluble in the usual organic solvents, but insoluble in water. The formation of this iodide is attended by the production of a small quantity of a *dodecane* (*dimethyldi*iso*butylethane*), $CH_2Pr^{\beta}\cdot CHMe\cdot CHMe\cdot CH_2Pr^{\beta}$, which forms a colourless, oily liquid with a faint odour, boils at 208—210°, and is soluble in light petroleum, and slightly so in alcohol. E. G.

Hexamethylethane. Louis Henry (*Compt. rend.*, 1906, **142**, 1075—1076).—*Hexamethylethane* (*ββγγ-tetramethylbutane*),

$$CMe_3\cdot CMe_3,$$

is an accessory product in the synthesis of pinacolyl alcohol by the interaction of acetaldehyde and magnesium *tert.*-butyl bromide. It crystallises from ether in barbed lamellæ, has a piquant, penetrating odour, melts at 103—104°, and boils at 106—107° under 765 mm. pressure. T. A. H.

Composition of Light Petroleum. Luigi Balbiano and Vincenzo Paolini (*Gazzetta*, 1906, **36**, i, 251—256. Compare Abstr., 1902, ii, 109).—Fourteen kilos. of American petroleum gave 3·5 grams of mercurous acetate when treated with mercuric acetate, whilst acetone and propaldehyde were found in the solution. These may have been formed by oxidation of β-methyl-Δ^{β}-pentylene.

T. H. P.

New Constituents of Coal Tar. Felix B. Ahrens (*Chem. Centr.*, 1906, i, 510—511; from *Verh. Ges. Deut. Naturforsch. Aerzte*, 1904, ii, 137—138. Compare Abstr., 1903, i, 515; 1904, i, 615; 1905, i, 232).—In a fraction from the benzene receiver which boiled at 20—30°, butylene and a compound which contained sulphur and resembled carbon disulphide, but was not identical with it, have been found. Amylene was isolated from a fraction boiling at 30—40°. 2 : 3-Dimethylpyridine has been obtained from a commercial sample of $\alpha\beta$-picoline; it boiled at 162—163° and yielded a picrate which melted at 183° and was almost insoluble in alcohol or water.

E. W. W.

Decomposition of Bromoform under the Influence of Light and Air.

Nicolaas Schoorl and L. M. van den Berg (*Chem. Centr.*, 1906, i, 441—442; from *Pharm. Weekblad*, **43**, 2—8. Compare this vol., i, 57).—When a current of air is passed through boiling bromoform in sunlight, bromine, hydrogen bromide, and carbon tetrabromide are produced. The primary reactions have already been investigated in the case of chloroform and iodoform. By the action of light in the presence of oxygen, carbon monoxide is oxidised to the dioxide, hydrogen bromide forms water and bromine, and by the action of the latter on bromoform, carbon tetrabromide and hydrogen bromine are obtained.

When bromoform, together with a small quantity of oxygen, is exposed to sunlight in sealed tubes, the action appears to result in the formation of carbon monoxide (1 mol.), bromine (1 mol.), and hydrogen bromide (1 mol.); when a large quantity of oxygen is present, carbon dioxide (2 mols.), water (1 mol.), and bromine (3 mols.) are formed. Carbon oxybromide is an intermediate product. When bromoform is exposed to sunlight in tubes from which the air has been almost completely removed, carbon monoxide and hydrogen bromide are obtained in the proportion of 13·7 to 47 1/10-equivalents; this result is consistent with the hypothesis that the bromoform is decomposed into carbon dibromide and hydrogen bromide, and that the former is decomposed by the water in the wash-bottles, forming carbon monoxide and hydrogen bromide. In addition to these products, 12 1/10-equivalents of bromine are also liberated. The liberation of bromine must be assumed to result from the intermediate formation of some other carbon hydrogen bromine compound, possibly of symmetrical tetrabromoethane, $CHBr_2,CHBr_2$, and the decrease of sp. gr. of the contents of the tube from 2·882 to 2·872 at 19° may be an indication of this change. The presence of carbon tetrabromide could not be detected in this case.

E. W. W.

Comparison of the Decomposition of Chloroform, Bromoform, and Iodoform under the Influence of Light

Nicolaas Schoorl and L. M. van den Berg (*Chem. Centr.*, 1906, i, 442; from *Pharm. Weekblad*, **43**, 8—10. Compare preceding abstract).—Experiments on the action of light alone on chloroform, bromoform, and iodoform have shown that whilst chloroform is not affected, iodoform is partially decomposed in consequence of the presence of traces of air, and bromoform is decomposed spontaneously, probably forming carbon dibromide and hydrogen bromide. By the action of air in the absence of sunlight at higher temperatures, iodoform becomes violet in a quarter of an hour, and the separation of iodine is distinctly visible in an hour; bromoform becomes acid and slightly yellow

in an hour, and gives a precipitate with silver nitrate, whilst chloroform does not give any reaction with silver nitrate after four hours.
E. W. W.

Decomposition of Iodoform dissolved in Chloroform by Diffused Daylight and by Radium Rays. WILLEM P. JORISSEN and WILHELM E. RINGER (*Chem. Centr.*, 1906, i, 442; from *Chem. Weekblad*, 2, 799—802. Compare preceding abstracts).—When a solution of iodoform in chloroform is exposed to diffused sunlight in the presence of oxygen, it appears to be completely decomposed. A solution of iodoform in carbon disulphide covered with water does not show any change for some time, and then decomposes only very slowly. A solution of iodoform in chloroform frozen by means of liquid air is not affected by bright daylight so long as it remains solid.

By the action of 5 mg. of radium bromide on 50 c.c. of a 1 per cent. solution of iodoform in chloroform at 25°, 75·2 per cent. of the iodine was liberated, whilst in a similar solution which was not exposed to the action of radium bromide only 18·8 per cent. of the iodine was found in a free state. The colour of the iodine solution formed by the action of the radium bromide was not so dark as that of similar solutions obtained by the action of daylight. E. W. W.

Abnormality in Melting Points of Amides derived from Aliphatic Sulphonic Acids. MAURICE DUGUET (*Bull. Acad. roy. Belg.*, 1906, 87—120).—iso*Propanesulphonic chloride*, $CHMe_2\cdot SO_2Cl$, prepared from phosphorus pentachloride and the corresponding alkali sulphonate, boils at 79° under 18 mm. pressure. Its solution in ether on treatment with dry ammonia yields the corresponding *sulphonamide*, which crystallises from ether on addition of light petroleum and melts at 60°. iso*Propanesulphonanilide* crystallises from a mixture of alcohol and water in colourless, pearly leaflets and melts at 84°. iso*Propanesulphon-α-naphthylamide* crystallises from a mixture of alcohol and water in slender needles and melts at 134°. *Butanesulphonic chloride* is a mobile, highly-refractive liquid, and boils at 96—97° under 18 mm. pressure. *Butanesulphonamide* crystallises from a mixture of ether and light petroleum in silky leaflets and melts at 45°. The corresponding *anilide* melts between −10° and −15° and the *α-naphthylamide* in colourless spangles melting at 60·5°.

Methanesulphon-α-naphthylamide crystallises in slender, silky needles and melts at 125—126°. *Ethanesulphon-α-naphthylamide* forms long, colourless prisms and melts at 66°. *Propanesulphon-α-naphthylamide* melts at 84°. iso*Butanesulphon-α-naphthylamide* crystallises in colourless spangles and melts at 107°. iso*Pentanesulphon-α-naphthylamide* forms colourless, pearly spangles and melts at 90—91°.

The melting points of the series of amides, anilides, and α-naphthylamides described in this and the former paper (Abstr., 1902, i, 428) decrease irregularly as each series is ascended; further, whilst the melting-point curve of the amides of the *iso*-acids is below that of the amides of the normal acids, the reverse is true of the curves for the anilides and α-naphthylamides of the *iso*- and *normal* acids. Similar examples of the fall in melting point as the series are ascended are shown by the aromatic sulphonamides (Abstr., 1900, i, 147) and the halogen and other derivatives of these described by Chattaway (Trans., 1905, 87, 145). Determinations of the molecular weights of the lower members of the series of compounds now described indicate that in dilute solutions they are not polymerised, but it is not certain that their high melting points are not the result of polymerisation in the solid state. It is pointed out also that there is a possibility of tautomerism in these compounds between the forms $R\cdot SO_2\cdot NH_2$ and $R\cdot SO(OH)\colon NH$, and that eventually each may be found to exist in two forms having different melting points. Thus, in the case of *iso*propanesulphonamide, one specimen prepared from *iso*propanesulphonic chloride, which had been kept for seven years, melted at 19—20° instead of 60°, but so far it has proved impossible to repeat this experience in the case of this or any other sulphonamide. T. A. H.

Influence of Oxidation of Ethyl Alcohol on the Maturing of Brandy and Wine. Auguste Trillat (*Chem. Centr.*, 1906, i, 580—581; from *Bull. Assoc. Chim. Sucr. Dist.*, 1905, 23, 495—503).—In confirmation of the results obtained by previous workers, it is shown that ethyl, propyl, butyl, and amyl alcohols are readily oxidised spontaneously to acetals, especially in the presence of ferric chloride or hydrochloric acid. Having found that acetals give a blue or green coloration with dimethylaniline and dilute sulphuric acid, owing probably to the formation of compounds of the type $NMe_2\cdot C_6H_4Me\cdot CH\cdot C_6H_4\cdot NMe_2$, the author has employed the reaction in detecting acetals in a number of brandies and liqueurs, and suggests that the maturing of spirits and wines is due partly to the formation of these acetals, which are highly aromatic substances, and partly to the formation of esters. It has been shown that *Mycoderma vini* materially increases the amount of aldehyde in wine, with the result that the wine becomes turbid, loses its colour, and in the presence of potassium salts may even acquire a bitter taste. P. H.

Constitution of Pinacolin and its Derivatives. Maurice Delacre (*Bull. Acad. roy. Belg.*, 1906, 7—41. Compare Abstr., 1896, i, 591, 662; 1902, i, 79).—The solid chloride, $CMe_3\cdot CMeCl_2$, obtained by the action of phosphorus pentachloride on pinacolin, is now shown to be identical with Faworsky's chloride, since both on treatment with alcoholic potash furnish the same unsaturated liquid chloride, $CMe_3\cdot CCl\colon CH_2$. The existence of an isomeride (boiling point 93°) of this unsaturated chloride, obtained by the action of alcoholic potash on the by-products of the action of phosphoric chloride on pinacolin, is confirmed. By the action of sodium on the liquid chloride, $CMe_3\cdot CCl\colon CH_2$, γ-dimethyl-Δ^{α}-butylene is produced together with small quantities of an acetylenic hydrocarbon and a paraffin.

Primary pinacolyl acetate, $CMe_3\cdot CH_2\cdot CH_2\cdot OAc$, produced by the action of potassium acetate on the crude γ-dimethyl-Δ^{α}-butylene hydrobromide, obtained by the addition of hydrogen bromide to the impure hydrocarbon referred to above, is a colourless liquid, possessing an agreeable fruity odour and boiling at 153—157°. When hydrolysed with potassium hydroxide, it furnishes primary *pinacolyl alcohol*,

$CMe_3 \cdot CH_2 \cdot CH_2 \cdot OH$, which is colourless and mobile, has a faint aromatic odour, and solidifies between −60° and −65°. When treated with hydrogen bromide, the alcohol yields the corresponding *pinacolyl bromide*, and this is converted into pinacolyl acetate by potassium acetate, no isomerisation into the symmetrical isomeride taking place. Similarly, no isomerisation into a symmetrical isomeride is brought about by heating the bromide at 100° with hydrobromic acid or by treatment with alkalis. On oxidation with chromic acid, the alcohol yields a mixture of a new *hexoic acid* [*ββ-dimethylbutyric acid*], $CMe_3 \cdot CH_2 \cdot CO_2H$ (a colourless liquid boiling at 185—190°), and the corresponding *ββ-dimethylbutaldehyde*, $CMe_3 \cdot CH_2 \cdot CHO$, which boils at 100—112°.

The products described in the preceding paragraph are derived in the first instance from the hydrobromide prepared from the crude γ-dimethyl-Δ^{α}-butylene. If, however, this hydrocarbon in a pure state is treated with hydrogen bromide, it furnishes an additive product, which on treatment with potassium acetate yields no primary pinacolyl acetate, but only βγ-dimethyl-Δ^{β}-butylene, $Me_2C:CMe_2$, so that under these circumstances symmetrical isomerisation does occur. These results are in harmony with the abnormal cases recorded by Ipatieff and Dechanoff (Abstr., 1904, i, 705), and it may be assumed that the impurities associated with the crude hydrocarbon in this case exert the same action as the acetic acid employed as a solvent by Ipatieff and Dechanoff.

When the Grignard reaction is applied to *iso*propyl bromide and acetone, the principal product is probably $CHMe_2 \cdot CMe_2 \cdot OH$; this, like pinacolyl alcohol, boils at about 120°, and the corresponding bromide on treatment with alcoholic potash yields βγ-dimethyl-Δ^{β}-butylene.

When aldehyde is treated with magnesium *tert.*-butyl bromide crotonaldehyde, a crystalline *substance*, which boils at about 110°, and a *hexyl alcohol*, which may have the constitution $CMe_3 \cdot CHMe \cdot OH$, are produced. The hexyl alcohol boils at 116—125°; the corresponding *hexyl bromide* boils at 115—125°, and when treated with potassium acetate yields βγ-dimethyl-Δ^{β}-butylene.

The author discusses the "ketone" and "oxide" formulæ assigned to pinacolin in the light of these new results, and points out that neither is capable of giving a full explanation of the reactions of pinacolin and its derivatives, and that probably no single formula is capable of doing this. T. A. H.

Synthesis of Pentamethylethanol. Louis Henry (*Compt. rend.*, 1906, **142**, 1023—1024).—When ethyl chloro*iso*butyrate is treated with magnesium methyl bromide dissolved in ether, the pentamethylethanol, $CMe_3 \cdot CMe_2 \cdot OH$, of Butleroff (Abstr., 1875, 1248) is obtained. The chloride melts at 130°. T. A. H.

Mode of Formation of Polyhydric Alcohols. William Oechsner de Coninck (*Chem. Centr.*, 1906, i, 130; from *Rev. gén. Chim.*, 1905, **8**, 347).—The fermentation process by which glycerol is supposed to be formed in plant cells, namely, the reduction of formaldehyde according to the equation $3CH_2O + H_2 = C_3H_5(OH)_3$, may in a similar way give rise to other alcohols. If two atoms of hydrogen react with one, two, three, four, or five molecules of formaldehyde, methyl alcohol, glycol, glycerol, erythritol, or arabitol is formed. Higher members of the series may also be produced in the same manner. H. M. D.

Vegetable Lecithins. Ernst Winterstein and O. Hiestand (*Zeit. physiol. Chem.*, 1906, **47**, 490—498. Compare Abstr., 1904, ii, 141).—The vegetable lecithins vary in their percentage of phosphorus. They yield on hydrolysis, in addition to choline, fatty acids, and glycero-phosphoric acid, a considerable amount of sugar, in some cases as much as 16 per cent. The sugar is a mixture of hexoses and pentoses. It is thus doubtful if the vegetable lecithins are the same as those of animal origin. Whether there is any kephalin also is doubtful. It therefore appears wise to adopt the more general term phosphatides for these substances. W. D. H.

Difluorochloroacetic Acid. Frédéric Swarts (*Bull. Acad. roy. Belg.*, 1906, 42—51).—*Difluorochloroacetic acid*, $CClF_2\cdot CO_2H$, is prepared by exposing difluoroacetic acid (Abstr., 1903, i, 727) to the action of dry chlorine in sunlight. The action proceeds slowly, 12 grams of the acid being chlorinated in the course of a month. It fumes on exposure to air, has a strong odour, melts at 22·9°, and boils at 121·5°. In aqueous solution, the maximum electrical conductivity was found to be 392·3 and the coefficient of ionisation 99·66 at a dilution $N/256$. Comparison of these constants with those of trichloroacetic and fluorodichloroacetic acids shows that the substitution of chlorine by fluorine intensifies the acid character. The *potassium*, *barium*, and *silver* salts were prepared. The last-mentioned salt is very unstable, and is slowly hydrolysed by water, forming oxalic, hydrochloric, and hydrofluoric acids. The same decomposition of the silver salt takes place more slowly in alcohol, some ethyl difluorochloroacetate being also formed in this case. A similar hydrolysis of the alkali and alkaline-earth salts occurs in presence of excess of sodium hydroxide. This hydrolysis differs in character from that which takes place with other trihaloid acetic acids under similar conditions, these furnishing usually formic acid and a trihaloid methane. The author has observed a similar difference in the behaviour of the group $\cdot CCl_2F$ in toluene derivatives (compare Abstr., 1899, i, 197, and 1900, i, 637). T. A. H.

Indian Ghedda-wax Georg Buchner (*Chem. Zeit.*, 1906, **30**, 528—529).—In order to show that Ghedda-wax, obtained from the following species of Indian bees, *Apis indica*, *A. dorsata*, or *A. florea*, is in reality closely related to the ordinary beeswax of *Apis mellifica*, the author has determined the melting point, acid saponification, and iodine numbers of specimens of these various waxes, and the results obtained show that qualitatively they are all the same, any differences in composition being due only to the quantitative distribution of the various constituents. P. H.

Stereoisomerism in the Group of Unsaturated αβ-Acyclic Acids. Edmond E. Blaise and P. Bagard (*Compt. rend.*, 1906, **142**, 1087—1089).—It has been shown previously (Abstr., 1904, i, 369) that the distillation of α-hydroxy-acids in which the hydroxyl group is attached to a secondary carbon atom may be utilised for the preparation of aldehydes. This investigation has now been extended to α-hydroxy-acids in which the hydroxyl group is attached to a tertiary carbon, and it is found that the amount of ketone produced in this distillation decreases as the molecular weight of the acid increases; thus it varies from 48 per cent. in the case of α-hydroxy-α-methylpropionic acid to 5 per cent. in the case of α-hydroxy-α-ethylbutyric acid, and, conversely, the quantity of unsaturated acid simultaneously produced increases. The two acids here mentioned yield lactides, but the production of lactides ceases beyond the C_6 acids of the series.

When the unsaturated acid produced by distillation is capable of existing in two stereoisomeric forms, it is, as a rule, the less stable which preponderates, and this tendency grows as the series is ascended; thus, α-hydroxy-α-methylpropionic acid furnishes angelic and tiglic acids in about equal proportions, but α-hydroxy-α-ethylbutyric acid yields the less stable isomeride almost pure. In cases where a long chain is attached to the alcoholic carbon atom, there may be a migration of the ethylenic linking with the production of some βγ-unsaturated acid; this occurs in the distillation of α-hydroxy-α-propylvaleric acid. The unsaturated acids obtained by this reaction have been isolated and characterised by conversion into their amides by the method used by Bodroux (Abstr., 1904, i, 662).

The difference between the boiling points of two stereoisomeric unsaturated acids or of their esters decreases as the molecular weight increases. The relative stability towards reagents and heat of the less stable isomerides increases with the molecular weight; thus, whilst tiglic and angelic acids furnish the same bromide, the two ethylcrotonic acids yield different bromides. The less stable isomerides are very sensitive to the action of halogen acids, which transform them into the stable isomerides. Similarly, phosphorus trichloride transforms the less stable isomerides quantitatively into chlorides of the stable acids.

It is pointed out that *cis* and *trans* are no longer suitable descriptive prefixes for the two forms of unsaturated stereoisomeric acids, and it is suggested that they be replaced by the terms *labile* and *stable*, which are abbreviated by the author into *lab.* and *st.* T. A. H.

Ketone-cyanohydrins. A. J. Ultée (*Ber*, 1906, **39**, 1856—1858).—In reference to Bucherer and Grolée's work on this subject (this vol., i, 405), the author calls attention to prior work of his own (this vol., i, 5). C. S.

Equilibrium in the System, Glucinum Oxide, Oxalic Anhydride, and Water. Charles L. Parsons and Wm. O. Robinson (*J. Amer. Chem. Soc.*, 1906, **28**, 555—569).—Experiments are described which show that the only definite hydrated oxalates of glucinum are $GlC_2O_4,3H_2O$ and GlC_2O_4,H_2O. The oxalate, $GlC_2O_4,3H_2O$ (Rosenheim and Woge, Abstr., 1898, ii, 71), forms orthorhombic crystals [$a:b:c=0{\cdot}853:1{\cdot}0:1{\cdot}645$], and is soluble in less than its own weight of water at 100°, and but little less so at the ordinary temperature. The oxalate, GlC_2O_4,H_2O, is obtained by heating the trihydrate at 100—105°.

The acid oxalate described by Rosenheim and Woge (*loc. cit.*) could not be obtained, and the existence of any such salt is considered improbable.

The anhydrous oxalate cannot be obtained, since it is impossible to remove the last trace of water without simultaneously decomposing the oxalate.

An investigation of the so-called basic oxalates of glucinum has shown that these substances are not definite compounds, but consist of solid solutions of the oxalate in the hydroxide. E. G.

Reaction of Nitrous Anhydride with Ethyl Malonate.

RICHARD S. CURTISS (*Amer. Chem. J.*, 1906, **35**, 477—486. Compare Abstr., 1905, i, 507).—When the gases evolved by the action of warm nitric acid on arsenious oxide are passed into ethyl malonate at 0°, a green oil is formed which consists chiefly of ethyl mesoxalate, together with small quantities of ethyl *iso*nitrosomalonate and of oxalic and acetic acids and their esters. By suitable treatment, the green oil can be made to yield either ethyl oxomalonate, mesoxalic acid, or ethyl mesoxalate.

Ethyl mesoxalate can be thus obtained in a yield of 90 per cent. or more. It is volatile in the air, and distils under 40—50 mm. pressure without undergoing any marked decomposition, except the loss of water with formation of ethyl oxomalonate. One gram of water at 22° dissolves 1·3 grams; 1 gram of ethyl malonate dissolves 0·6 gram; and 1 c.c. of benzene at 22° dissolves 0·2 gram of the ester. The ester is also easily soluble in ether, acetone, chloroform, or alcohol.

If ethyl malonate is only partially saturated with the nitrogen oxides, ethyl *iso*nitrosomalonate is obtained; its potassium, *silver*, *sodium*, and *ammonium* salts are described. The observation of Baeyer (*Annalen*, 1864, **131**, 293) and of Conrad and Bischoff (Abstr., 1880, 629), that hydrogen cyanide is formed by the decomposition of *iso*nitrosomalonic acid in aqueous solution, could not be confirmed.

If pure crystalline ethyl mesoxalate is heated in a test-tube at its melting point (57°), water condenses on the cool part of the tube, and ethyl oxomalonate remains as a green oil. On cooling the tube and allowing the water to come into contact with the green oil, combination takes place immediately, the green colour disappears, and on touching the colourless liquid with a glass rod, the original crystalline substance is obtained.

Phenylhydrazine reacts with ethyl oxomalonate with formation of an amber-coloured *oil* which has acid properties and yields a yellow *potassium* salt. E. G.

Preparation of the Salts of Formaldehydesulphoxylic Acid.

BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 165807).—The salts of formaldehydesulphoxylic acid are obtained when the formaldehydebisulphite compounds or the product of the interaction of formaldehyde and a hyposulphite is treated with reducing agents. Dry sodium hyposulphite is dissolved in 40 per cent. aqueous formaldehyde and the solution heated to boiling for ten minutes with zinc dust and acetic acid. The zinc is then precipitated with sodium carbonate and the filtrate evaporated down under diminished pressure until a solid mass is obtained consisting of sodium formaldehydesulphoxylate mixed with a small proportion of sodium acetate. A similar result is produced by reducing the formaldehydebisulphite compound either with acetic acid and iron filings or aluminium powder, or with stannous chloride.

G. T. M.

Basic Properties of Oxygen. Additive Compounds of the Halogen Acids and Organic Substances containing Oxygen. DOUGLAS McINTOSH (*J. Amer. Chem. Soc.*, 1906, **28**, 588—590. Compare Trans., 1904, **85**, 919, 1098; 1905, **87**, 784; Abstr., 1905, i, 254, 677).—By the action of the halogen hydrides on acetaldehyde, acetic acid, and ethyl acetate at low temperatures, considerable heat is developed, and the following additive compounds are obtained, which are crystalline, melt sharply, and form supersaturated solutions in the liquid halogen hydride used in their preparation.

The *compound* $2CH_3{\cdot}CHO,3HCl$ melts at $-18°$, the *compound* $2CH_3{\cdot}CO_2H,3HCl$ at $-53°$, and the *compound* $CH_3{\cdot}CO_2Et,2HCl$ at $-75°$. The methyl alcohol *compound*, $3CH_3{\cdot}OH,2HCl$, melts at $-64°$.

The *compound* $2CH_3{\cdot}CHO,3HBr$ melts at $-15°$, and the *compound* $2CH_3{\cdot}CO_2Et,3HBr$ at $-40°$. Acetic acid does not unite with hydrogen bromide or iodide at low temperatures.

The *compound* $3CH_3{\cdot}CHO,2HI$ melts at $-32°$, and the *compound* $CH_3{\cdot}CO_2Et,HI$ at $-23°$. E. G.

Decomposition of Chloral Hydrate by Exposure to Light and Air. NICOLAAS SCHOORL and L. M. VAN DEN BERG (*Chem. Centr.*, 1906, i, 650; from *Pharm. Weekblad*, 1906, **43**, 42—47).—Chloral hydrate, when exposed to tropical sunlight in an exhausted tube, is decomposed according to the following equation: $CCl_3CHO,H_2O = 3HCl + 2CO$. When sealed up in tubes containing an insufficient supply of oxygen, a portion of the substance is also decomposed as follows: $CCl_3CHO,H_2O + 2O = 3HCl + 2CO_2$, although it may be that the carbon dioxide is only formed by the subsequent oxidation of the monoxide produced according to the first equation. In the presence of an excess of oxygen, the following decompositions take place: $CCl_3CHO,H_2O + 2O = 3HCl + 2CO_2$ and $2CCl_3CHO,H_2O + 7O = 3H_2O + 6Cl + 4CO_2$. P. H.

A Soluble Polychloral. SIMON GÄRTNER (D.R.-P. 165984).—By treating chloral with pyridine or other amines in the cold and then acidifying the product, a stable, homogeneous polymeride of chloral is obtained, which retains the soporific action of the simple aldehydehydrate, but is less poisonous, and differs from the polychlorals previously described in dissolving in water or alcohol, slowly at the ordinary temperature and rapidly on boiling, to yield respectively chloral hydrate or chloral alcoholate.

If trimethylamine is employed to induce this polymerisation, it should be used in dilute solutions of inert solvents, otherwise the reaction is very violent and an ill-defined heterogeneous product is obtained. G. T. M.

Condensation of Ketones with Cyanoacetic and Malonic Acids. Emil Knoevenagel (D.R.-P. 162281. Compare Abstr., 1905, i, 169; also Komppa, Abstr., 1901, i, 114).—Acetone condenses with cyanoacetic acid in presence of piperidine hydrochloride on the water-bath, forming *α-cyano-ββ-dimethylacrylic acid*,

$$\mathrm{CMe_2{:}C(CN){\cdot}CO_2H},$$

melting at 130°. Acetophenone and cyanoacetic acid give *α-cyano-β-phenyl-β-methylacrylic acid*, $\mathrm{CPhMe{:}C(CN){\cdot}CO_2H}$, melting at 135—136°. Mesityl oxide and cyanoacetic acid give the *acid*,

$$\mathrm{CMe_2{:}CH{\cdot}CMe{:}C(CN){\cdot}CO_2H},$$

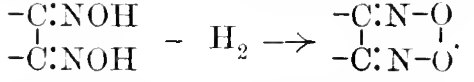
melting at 96°. When acetone and cyanoacetic acid are heated for a long time with ethylamine, carbon dioxide is evolved, and *αγ-dicyano-ββ-dimethylbutyric acid*, $\mathrm{CN{\cdot}CH_2{\cdot}CMe_2{\cdot}CH(CN){\cdot}CO_2H}$, melting at 196—197°, is formed. Acetone and malonic acid yield ββ-dimethylacrylic acid. C. H. D.

Behaviour of Acetoxime and of Dioximes towards Sodium Hypochloride. Properties of Carbon Tetrabromide. Giacomo Ponzio (*Atti R. Accad. Sci. Torino*, 1906, **41**, 415—426).—The action of sodium hypochlorite on acetoxime yields, not acetoxime hypochlorite, as was stated to be the case by Möhlau and Hofmann (Abstr., 1887, 795), but firstly β-chloro-β-nitrosopropane, which afterwards undergoes oxidation to β-chloro-β-nitropropane. *β-Chloro-β-nitrosopropane*,

$$\mathrm{CMe_2Cl{\cdot}NO},$$

has a pungent odour and the characteristic blue colour of nitrolic liquid compounds, and under 18 mm. pressure boils at about 7° giving a colourless vapour, whilst under the ordinary pressure it boils and decomposes at about 68°.

With sodium hypochlorite, *p*-quinonedioxime gives *p*-dinitrobenzene and β-naphthaquinonedioxime yields 1 : 2-dinitrosonaphthalene, whilst the dioximes of benzyl and of camphoquinone are transformed into the corresponding peroxides. The reaction between sodium hypochlorite and the dioximes may be regarded as the elimination of two atoms of hydrogen from the dioxime, with formation of a cyclic compound :



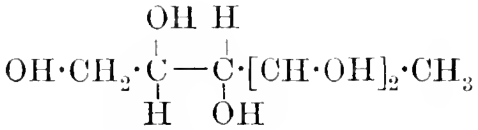
$$\begin{array}{l}\mathrm{-C{:}NOH}\\ \mathrm{-C{:}NOH}\end{array} - \mathrm{H_2} \longrightarrow \begin{array}{l}\mathrm{-C{:}N{-}O}\\ \mathrm{-C{:}N{-}O}\end{array}.$$

The mode of action of sodium hypochlorite on the dioximes is hence similar to that of potassium ferricyanide, with the advantages that the oxidation takes place almost instantaneously and in the cold, that a theoretical yield is obtained, and that the products do not require the tedious purification necessary when ferricyanide is employed.

A simple method of preparing carbon tetrabromide consists in dissolving 10 grams of acetone in 10 litres of water, adding 180 grams of bromine and 1500 c.c. of a 30 per cent. solution of sodium hydroxide, and allowing to remain. It can also be obtained by the action of sodium hypobromite on diacetyldioxime, methylethylketoxime, *iso*nitrosomethyl ethyl ketone, or *iso*nitrosocamphor. It exhibits the following reactions (compare Bolas and Groves, this Journal, 1871, **29**, 782). When heated with water in a sealed tube at 200°, it is completely decomposed into carbon dioxide and hydrogen bromide, according to the equation $CBr_4 + 2H_2O = CO_2 + 4HBr$. When heated with alcohol in a sealed tube at 150°, carbon tetrabromide yields ethyl bromide, bromoform, and traces of acetaldehyde; when 80 per cent. alcohol is used, the action begins at 100°. With sodium ethoxide in ethereal solution, carbon tetrabromide gives ethyl orthocarbonate. When heated with aniline, carbon tetrabromide yields aniline hydrobromide, whilst with aniline and alcoholic potassium hydroxide solution phenylcarbylamine is obtained. Phenylhydrazine hydrobromide may be readily prepared by adding phenylhydrazine to an ethereal solution of carbon tetrabromide cooled in ice; if alcoholic potassium hydroxide is present, phenylcarbylamine is formed. T. H. P.

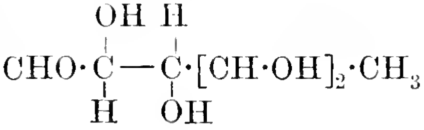
Rhodeitol. Emil Votoček and J. Bulíř (*Zeit. Zuckerind. Böhm.*, 1906, **30**, 333—339).—Rhodeose, previously prepared from convolvulin (Abstr., 1900, i, 332) may be more cheaply obtained by heating powdered jalap resin (Resina jalapae e radice ponderosa) with barium hydroxide solution to dissolve the glucoside and leave the resin unchanged, removing the barium hydroxide, and hydrolysing by means of 10 per cent. sulphuric acid solution.

Rhodeitol, $C_6H_{14}O_5$, best prepared by reducing rhodeose by means of 2·5 per cent. sodium amalgam in a solution kept alkaline to an extent not exceeding 0·5 per cent. of sodium hydroxide, crystallises from alcohol in silky, white plates melting at 153·5° and is readily soluble in water; it can be distilled, reduces Fehling's solution, and has $[\alpha]_D$ − 1·45° in aqueous solution or − 4·6° in 10 per cent. borax solution at 21°. Oxidation of rhodeitol by means of bromine in sodium carbonate solution or of nitric acid yields a ketose (rhodeoketose) but no aldose. Rhodeitol is not oxidised by the sorbose bacterium (compare Bertrand, Abstr., 1898, i, 550), so that it must have either the formula



$$\mathrm{OH{\cdot}CH_2{\cdot}\overset{OH}{\underset{H}{C}}\text{—}\overset{H}{\underset{OH}{C}}{\cdot}[CH{\cdot}OH]_2{\cdot}CH_3}$$

or the enantiomorphous one. The constitution of rhodeose must hence be represented by $\mathrm{CHO{\cdot}\overset{OH}{\underset{H}{C}}\text{—}\overset{H}{\underset{OH}{C}}{\cdot}[CH{\cdot}OH]_2{\cdot}CH_3}$ or by the mirror-image of this formula.



A mixture of equal proportions of the two optical antipodes, rhodeose and fucose, gives on reduction with sodium amalgam a true racemic compound, r-*rhodeitol* or r-*fucitol*, $C_6H_{14}O_5$, which crystallises in shining plates melting at 168° and dissolves readily in water and sparingly in alcohol. T. H. P.

The almost complete Conversion into Maltose of the Dextrins obtained by the Saccharification of Starch. AUGUSTE FERNBACH and JULES WOLFF (*Compt. rend.*, 1906, **142**, 1216—1218. Compare Maquenne and Roux, this vol., i, 327).—At a temperature of 50°, starch is almost completely converted into maltose by the action of malt extract, and the second stage of the reaction, namely, the conversion of the dextrin into maltose, is accelerated by adding acid until the liquid is neutral to methyl-orange. Under these conditions, 300 c.c. of a solution containing 13 grams of starch and 50 c.c. of a 10 per cent. malt extract yielded after ninety-four hours 103·8 grams of maltose per 100 grams of starch, or 1·7 per cent. less than the theoretical quantity; the solution contained 1·9 per cent. of dextrin which had escaped saccharification owing to the dilution. If, however, the dextrin is precipitated by alcohol and then subjected to the further action of malt extract, it is slowly converted into maltose.

M. A. W.

Combinations of Mercuric Iodide and Methylamine. MAURICE FRANÇOIS (*Compt. rend.*, 1906, **142**, 1199—1202. Compare Abstr., 1905, i, 574).—Mercuric iodide readily combines with gaseous methylamine at the ordinary temperature to form the liquid $5NH_2Me,HgI_2$, which by loss of methylamine forms successively the solid compounds $2NH_2Me,HgI_2$ and NH_2Me,HgI_2.

Pentamethylaminomercuric iodide, $5NH_2Me,HgI_2$, most conveniently prepared in a pure state by the action of methylamine on the compound, $2NH_2Me,HgI_2$, forms a colourless liquid which solidifies at − 46°, can be preserved indefinitely in sealed tubes, but loses methylamine when exposed to the air, the dissociation pressure at 0° being 280 mm. and becoming atmospheric at 25°.

Dimethylaminomercuric iodide, $2NH_2Me,HgI_2$, obtained from the preceding compound by partial loss of methylamine, or by adding an excess of methylamine solution to a saturated solution of mercuric iodide in potassium iodide, forms colourless prisms sometimes 10 cm. long, with an ammoniacal odour.

Methylaminomercuric iodide, NH_2Me,HgI_2, is obtained from the preceding compound by subjecting it at the ordinary temperature to a current of air for twelve hours, or by placing a capsule containing a weighed quantity of the compound, $2NH_2Me,HgI_2$, in a closed vessel containing mercuric iodide, or by pouring a solution of methylamine into excess of a saturated solution of mercuric iodide in potassium iodide; the compound is a yellowish-white solid which yields red mercuric iodide on prolonged exposure to the air. M. A. W.

Synthesis of Secondary Mixed Amines by Hinsberg's Method. A. MULDER (*Rec. trav. chim.*, 1906, **25**, 104—107).—The author has prepared methylpropylamine, ethylpropylamine, and ethyl*iso*propylamine by the general method described by Hinsberg (Abstr., 1892, i, 64). Good yields were obtained except in the case of ethyl*iso*propylamine, and it appears that Hinsberg's method is not suited to the preparation of mixed amines containing a secondary carbon atom.

Benzenesulphonmethylpropylamide, $SO_2Ph\cdot NMePr^a$, obtained by the action of propyl iodide on the potassium derivative of benzenesulphonmethylamide, $SO_2Ph\cdot NMeK$, is a colourless oil and boils at 184—186 under 21 to 24 mm. pressure. *Benzenesulphonethylpropylamide*, similarly obtained, boils at 229—231° under 26 to 33 mm. pressure. *Benzenesulphonethylisopropylamide* is crystalline, melts at 51—52°, and is readily soluble in the usual solvents with the exception of water and light petroleum. T. A. H.

Action of Ethylenediamine on Cobalt and Platinum Compounds. Hermann Grossmann and Bernhard Schück (*Ber.*, 1906, **39**, 1896—1901).—Werner and Bräunlich (Abstr., 1900, i, 86), by the action of varying amounts of potassium thiocyanate on dichlorodiethylenediamine cobaltichloride, have prepared the isomerides $[Co(C_2H_8N_2)_2(S\cdot C\vdots N)_2]Cl$ and $[Co(C_2H_8N_2)_2(N\colon C\colon S)_2]Cl$, the existence of which depends on the tautomerism exhibited by thiocyanic acid. The authors have prepared compounds of the *iso*thiocyano-series by a simpler method than Werner and Bräunlich's and quite free from the isomeric thiocyano-salts by passing air through an aqueous solution of a mixture of ethylenediamine (2 mols.) and cobalt thiocyanate (1 mol.) on a boiling water-bath until the solution becomes carmine-red. Glistening, ruby-red needles of the di*iso*rhodanato-salt, previously described by Werner and Bräunlich, separate.

Triethylenediamine cobaltithiocyanate, $(Co,3C_2H_8N_2)(SCN)_3$, prepared by heating an aqueous solution of ethylenediamine (3 mols.) and cobalt thiocyanate (1 mol.), forms golden-yellow, glistening crystals and melts at 211°. It gives the characteristic coloration with ferric chloride. On the addition of potassium cyanide, the solution becomes yellowish-red and, on cooling, the luteocyanide separates in cubical crystals melting at 240°.

The *bromide*, $(Co,3C_2H_8N_2)Br_3,2H_2O$, prepared by the action of ethylenediamine (2 mols.) on cobalt bromide (1 mol.), forms yellow needles and melts and decomposes at 271°.

Dibromodiethylenediamine cobaltithiocyanate, $[Co(C_2H_8N_2)_2]SCN,H_2O$, prepared by the action of potassium thiocyanate on a cold saturated solution of the praseobromide, $[Co(C_2H_8N_2)_2Br_2]Br$, forms green crystals, the aqueous solution of which changes from green to red when boiled with water.

The *compound*, $[Pt(C_2H_8N_2)(SCN)_2](SCN)_2$, prepared by the action of ethylenediamine on potassium platinic thiocyanate, $K_2Pt(SCN)_6$, forms yellow crystals and melts at 141°.

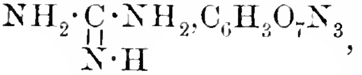
The *compound*, $[Pt(C_2H_8N_2)_2](SCN)_2$, prepared in an analogous manner from potassium platinous thiocyanate, $K_2Pt(SCN)_4$, forms orange-yellow crystals and melts at 177°. A. McK.

Bromodialkylacetamides. Kalle & Co. (D.R.-P. 166359).—Bromodiethylacetamide, $CEt_2Br\cdot CO\cdot NH_2$ or $CEt_2Br\cdot C(NH)\cdot OH$, was prepared by adding very slowly the calculated amount of bromine to diethylacetamide dissolved in water; the product is extracted with ether recrystallised from dilute alcohol. A similar bromo-derivative was obtained from ethylpropylacetamide. G. T. M.

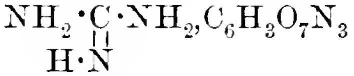
Hydroxymethyl Derivatives of Amides. Alfred Einhorn (D.R.-P. 162395. Compare Abstr., 1905, i, 646; this vol., i, 245).—The method of preparation of hydroxymethyl derivatives from aromatic amides is not applicable to fatty amides unless containing substituted halogen. Thus, chloroacetamide readily reacts at 100° with formaldehyde in presence of concentrated hydrochloric acid. The product is evaporated in a vacuum after neutralising with sodium acetate, and the resulting syrup crystallised from acetone.

C. H. D.

Probable Stereoisomerism of Nitrogen in Guanidine Picrate. Victor von Cordier (*Chem. Centr.*, 1906, i, 340; from *Verh. Ges. Deut. Naturforsch. Aerzte*, 1904, ii, 105—108).—Guanidine picrate is usually obtained in the form of dark yellow plates which, owing to repeated twinning, have a book-like structure, but when guanidine which has been prepared by the decomposition of methyl guanidine sulphate by means of barium hydroxide is used, the picrate crystallises in rosettes of bright yellow needles. Both forms have the same composition, temperature of decomposition, sp. gr., and electrical conductivity, but whilst 100 parts water dissolve 0·037 part of the plates at 0°, 0·061 at 20°, and 0·574 at 80°, the solubility of the needles is 0·043, 0·060, and 0·800 at these temperatures respectively. One form cannot be obtained from the other by crystallisation. When either is converted into the carbonate or other salt, or even into derivatives such as glycocyamine, guanidinesarcosine hydrochloride, &c., and the picrate again prepared, it usually crystallises in the original form. Under certain conditions, however, it is possible to obtain the crystalline plates from the carbonate or glycine compound which has been prepared from needles of the picrate, but the reverse change has not been observed. Both forms are optically inactive, and are probably stereoisomerides, the plates being the stable modification



$NH_2\cdot\underset{\underset{N\cdot H}{\|}}{C}\cdot NH_2,C_6H_3O_7N_3$, and the needles the labile,



$$NH_2\cdot\underset{\underset{H\cdot N}{\|}}{C}\cdot NH_2,C_6H_3O_7N_3\,.$$

E. W. W.

Preparation of Hydrogen Cyanide from Ferrocyanides. Walther Feld (D.R.-P. 162362).—Sufficient calcium hydroxide or carbonate is added to a solution of calcium ferricyanide to combine with all the iron present; mercuric chloride is then added, together with magnesium chloride, to prevent the precipitation of mercuric oxide, and the whole is boiled. The reaction is $Ca_3(FeCy_6)_2 + 3Ca(OH)_2 + 6HgCl_2 = 6HgCy_2 + 6CaCl_2 + Fe_2(OH)_6$. The precipitate is filtered off and the solution distilled with sulphuric acid. Ferrocyanides are previously oxidised to ferricyanides with bleaching powder and sulphuric acid.

C. H. D.

Reduction of Potassium Ferricyanide. Domenico Venditori (*Atti R. Accad. Lincei*, 1906, [v], 15, i, 370—373).—Potassium ferricyanide is reduced by hydrogen sulphide, slowly at the ordinary temperature, rapidly on heating, the reaction being expressed by the equation $6K_3FeCy_6 + 3H_2S = 4K_4FeCy_6 + K_2Fe_2Cy_6 + 6HCN + 3S$. These results differ from those obtained by Williamson (*Annalen*, 1846, **57**, 237).

T. H. P.

Ferricyanides of Mercury. Gustave Fernekes (*J. Amer. Chem. Soc.*, 1906, **28**, 602—605).—*Mercuric ferricyanide*, $Hg_3Fe_2(CN)_{12}$, obtained by adding a concentrated aqueous solution of potassium ferricyanide to a solution of mercuric chloride in alcohol and ether and washing the precipitate with alcohol and ether, is a bright yellow substance which is fairly stable when dry, but rapidly undergoes decomposition in aqueous solution with formation of hydrogen cyanide and a blue substance, which is probably Prussian blue.

Mercurous ferricyanide, $Hg_3Fe(CN)_6$, is obtained as a flocculent, cream-coloured precipitate when a solution of mercurous nitrate is added to a solution of potassium ferricyanide, and turns blue on exposure to the air.

E. G.

Oxidation of Chromous Salts. Julius Sand and O. Burger (*Ber.*, 1906, **39**, 1771—1779. Compare Abstr., 1903, ii, 549; 1904, ii, 39; Kohlschütter, *ibid.*, ii, 737).—When nitric oxide is passed into a moist amyl-alcoholic solution of chromous thiocyanate and excess of ammonium thiocyanate, an opaque, dark red solution is obtained which can be concentrated on the water-bath. After removal of the alcohol, the purple residue is recrystallised from hot concentrated ammonium hydroxide; it separates in glistening needles which have the composition $O[Cr(SCN)_2]_2,4NH_3$. The ammonia is only loosely bound, being eliminated by dilute hydrochloric acid, and from the conductivity and cryoscopic behaviour of the solution the residual, $Cr_2(SCN)_4O$, functions as a binary electrolyte. Nitrous acid precipitates unstable black crystals from an ice-cold solution of the substance in dilute sulphuric acid. From a dilute hydrochloric acid solution, pyridine and water precipitate violet-grey crystals having the composition $Cr_2(SCN)_4O(C_5H_5N)_4$.

When the oxidation of the amyl-alcoholic solution of chromous thiocyanate and excess of ammonium thiocyanate is performed in the presence of pyridine by nitric oxide, ammonium persulphate, or alcoholic iodine, a very stable *substance*, $Cr(SCN)_4(C_5H_5N)_2,H(C_5H_5N)$, is obtained, which is not attacked by acidified hydrogen peroxide or by chlorine and boiling hydrochloric acid. With alcoholic pyridine, it forms a *substance*, $[Cr(SCN)_4(C_5H_5N)_2(C_5H_5N)]H(C_5H_5N)$, in harmony with the co-ordination theory.

The action of nitric oxide on chromous salts in ammonium carbonate solution leads to the formation of a basic chromammonium carbonate, $Cr(NH_4)(OH)_2CO_3$.

C. S.

Reduction of Molybdic Acid in Thiocyanic Acid Solution. Julius Sand and O. Burger (*Ber.*, 1906, **39**, 1761—1770. Abstr., 1905, i, 923; Chilesotti, this vol., ii, 263, 365).—Through a solution of ammonium molybdate and excess of ammonium thiocyanate in dilute hydrochloric acid a current of 1·95 amperes is passed until two farads have been utilised for each gram-mol. of molybdic acid, the platinum cathode being smooth and of 300 sq. cm. area. The reduced liquid is treated with ether, pyridine added until the ethereal layer is colourless, the red oil is separated and boiled with alcohol. The brown, crystalline residue is described subsequently. The alcoholic solution by treatment with excess of ether deposits a yellow oil, soluble in ammonium hydroxide and reprecipitated by cold acid in yellow crystals of *molybdenumtetrapyridinehexathiocyanic acid*,

$$H_2[Mo(SCN)_6(C_5H_5N)_4],$$

which readily loses pyridine and is best purified by precipitation from potash solution by carbon dioxide. When treated with pyridine in methyl-alcoholic solution, it yields the hexathiocyanate previously described (*loc. cit.*). After the action of hydrogen chloride on the acid in acetone, ether precipitates amber-yellow crystals of the composition $Mo(SCN)_6(C_5H_5N)_4H_2(C_5H_5N),2HCl$, which melt at 141°.

The *zinc*, *nickel*, and *copper* salts precipitated from ammoniacal solution contain $(NH_3)_4$ in the place of $(C_5H_5N)_4$; the zinc salt, $Zn[Mo(SCN)_6(NH_3)_4]$, crystallises from hot concentrated ammonium hydroxide in glistening needles and is especially characteristic. The *silver* salt, $Ag_2[Mo(SCN)_6(C_5H_5N)_4]$, is precipitated from methyl-alcoholic and pyridine solution in yellow crystals.

Evidence is quoted which indicates that the molybdenum in these compounds functions as a quadrivalent element.

The brown crystals previously mentioned separate from hot alcohol in aggregates of brown, feathery crystals which melt and decompose at 182°. They were previously described as having the composition $Mo[(C_5H_5N)_2(SCN)_4]$ (*loc. cit.*), but are now found to be $Mo(OH)_2(SCN)_3(C_5H_5N)_2$. The chloride is $MoOCl_3(C_5H_5N,HCl)_2$, not $Mo(C_5H_5N,HCl)_6Cl_4$ (*loc. cit.*), and is easily hydrolysed in dilute alcohol to a basic *salt*, $Mo(OH)_3Cl_2,C_5H_5N$. The brown molybdenumdihydroxydipyridinetrithiocyanate does not react with atmospheric oxygen; with 20 per cent. sulphuric acid, it forms a purple solution from which dark green crystals, $[Mo(OH)(C_5H_5N)_2(SCN)_3]_2SO_4$, separate.
C. S.

New Methods of preparing some Organic Derivatives of Arsenic. VICTOR AUGER (*Compt. rend.*, 1906, **142**, 1151—1153. Compare Abstr., 1904, i, 22, 724, 983).—Starting with methylarsonic acid or cacodylic acid, which are commercial products, the following organic derivatives of arsenic can be readily prepared: methylarsine di-iodide, $AsMeI_2$, obtained by reducing methylarsonic acid with sulphur dioxide and treating the product with potassium iodide and hydrochloric acid, the yield is 82 per cent. of the theoretical, and it is converted quantitatively into methylarsine oxide, AsMeO, by heating a solution in benzene with dry sodium carbonate; methylarsine dichloride, $AsMeCl_2$, prepared by adding methylarsonic acid to phosphorus trichloride, contains a small quantity of arsenic trichloride; cacodyl chloride, $AsMe_2Cl$, obtained with an excellent yield by distilling a mixture of sodium hypophosphite, cacodylic acid, and hydrochloric acid, $2AsMe_2O_2H + 3H_3PO_2 + 2HCl = 3H_3PO_3 + H_2O + 2AsMe_2Cl$, or by the action of phosphorus trichloride on cacodylic acid, is converted into cacodylic oxide by the action of dry sodium carbonate; cacodyl, As_2Me_4, is readily prepared by the action of excess of sodium hypophosphite on cacodylic acid in hydrochloric acid solution; tetramethylarsonium iodide, $AsMe_4I$, obtained by the action of hypophosphorus acid and methyl iodide on cacodylic acid according to the equation $AsMe_2O_2H + 2MeI + 2H_3PO_2 = AsMe_4I + 2H_3PO_3 + HI$.

M. A. W.

Preparation and Properties of Individual Organo-magnesium Compounds. WLADIMIR TSCHELINZEFF (*Chem. Zeit.*, 1906, **30**, 378—379. Compare this vol., ii, 334, 335).—Magnesium alkyl compounds of the type R·Mg·R are solid substances which decompose on heating without melting; they are soluble in a mixture of ether and benzene, and can be recovered from this solution unchanged. They catch fire and explode in contact with water, carbon dioxide, or oxygen, and react with ketones, aldehydes, or esters to form complex substances which are decomposed by water with the formation of hydrocarbons. Compounds of the type RMgI are solids which dissolve in ether or a mixture of ether and benzene, but cannot be recovered from the solution; they react less violently with water, carbon dioxide, or oxygen, and with ketones, aldehydes, or esters they yield compounds which do not evolve hydrocarbons on treatment with water.

P. H.

Problem of Substitution in the Benzene Ring. ARNOLD F. HOLLEMAN (*Chem. Centr.*, 1906, i, 457—459; from *Chem. Weekblad*, **3**, 1—11. Compare Abstr., 1903, i, 336, 623; 1904, i, 486; 1905, i, 41, 42, 515).—The problem of substitution in the benzene ring is discussed at length in the abstract, and some of the work of the author published already on the nitration of benzene derivatives is quoted. For further details, the abstracts or original paper should be consulted.

E. W. W.

Optically Active Benzene Hydrocarbons. III. AUGUST KLAGES and RICHARD SAUTTER (*Ber.*, 1906, **39**, 1938—1942. Compare Abstr., 1904, i, 302; 1905, i, 579).—*α-Hydroxy-γη-dimethyl-Δ^η-octenylbenzene*, $OH{\cdot}CHPh{\cdot}CH_2{\cdot}CHMe{\cdot}[CH_2]_3{\cdot}CMe{:}CH_2$, prepared by the action of acetic acid and ice on the product of the reaction of magnesium phenyl bromide with citronellaldehyde, is a colourless oil, which boils at 174° under 9·5 mm. pressure, has a sp. gr. 0·9469 at 15·5°/4°, n_D 1·5137 at 15·5°, and $[\alpha]_D$ $-1{\cdot}56°$ at 15·5°. The carbinol obtained on treatment of the reaction product with ice only has a higher specific rotation.

γη-Dimethyl-$\Delta^{a\eta}$-octadienylbenzene,

$$CHPh{:}CH{\cdot}CHMe{\cdot}[CH_2]_3{\cdot}CMe{:}CH_2,$$

is formed by treating the carbinol with hydrogen chloride in ethereal solution cooled by ice, and heating the *dichloride*, $C_{16}H_{24}Cl_2$, so formed, which has n_D 1·5168 and $[\alpha]_D$ $-9{\cdot}06°$ at 11·5°, with pyridine for five hours. It is a colourless, odourless, strongly refracting oil, which boils at 152° under 9·5 mm. pressure, has a sp. gr. 0·8947 at 17°/4°,

n_D 1·5276, and $[\alpha]_D$ −65·11° at 17°, and reacts with bromine in the cold, forming an oily *tetrabromide*, $C_{16}H_{22}Br_4$, together with small amounts of bromo-derivatives.

When heated with oxalic acid, the carbinol yields 1-*phenyl-5-methyl-2-isopropenylcyclohexane*, $C_6H_9MePh\cdot CMe\colon CH_2$; this is obtained as a colourless, mobile oil, which boils at 139—140° under 10 mm. pressure, has a sp. gr. 0·9462 at 15·7°/4°, n_D 1·5802, and $[\alpha]_D$ +17°.

γη-Dimethyl-Δ^η-octenylbenzene, $C_{16}H_{24}$, is formed by reduction of γη-dimethyl-$\Delta^{\alpha\eta}$-octadienylbenzene by means of sodium and alcohol, boils at 145—146° under 9·5 mm. pressure, has a sp. gr. 0·8844 at 11·5°/4°, n_D 1·5029, and $[\alpha]_D$ −7·26°.

γη-Dimethyloctylbenzene, $C_{16}H_{26}$, prepared by reducing the preceding substance with hydriodic acid and red phosphorus in a sealed tube at 160°, is obtained as a colourless, miscible oil which boils at 275° (corr.) or at 140° under 8·5 mm. pressure, and has a sp. gr. 0·8789 at 10·5°/4°, n_D 1·4960, and $[\alpha]_D$ −1·82° at 10·5°. When treated with sulphuric acid containing 6 per cent. of sulphuric anhydride, it yields an oily *sulphonic acid*, which is soluble in water, and with sodium chloride gives a voluminous precipitate of the *sodium* salt. G. Y.

Bromination of Toluene. F. H. van der Laan (*Chem. Centr*, 1906, i, 661—662; from *Chem. Weekblad*, 1906, **3**, 15—21).—The author has made quantitative measurements with a view to determining the influence of temperature, of bromine carriers, or of light on the yield of *o*- or *p*-bromotoluene or benzyl bromide. Below 17°, no benzyl bromide is formed, whereas above 83° it is formed exclusively. Antimony tribromide only slightly increases the yield of ring-substituted derivatives, and appears rather to favour the formation of the para-form. Five mg. of aluminium added to 3 c.c. of bromine completely prevent the formation of benzyl bromide, and increase the yield of the *o*-variety as compared to the *p*-, whereas 2 mg. of aluminium are without effect. Ferric bromide has a similar although rather more marked effect than aluminium bromide. The action of aluminium amalgam is similar to that of aluminium bromide. The addition of 0·02 mol. of phosphorus pentabromide to 1 mol. of bromine gives, at 50°, 10 per cent. more benzyl bromide than in the absence of a halogen carrier. In diffused daylight, bromination takes place more rapidly. A reaction which at 25° is not completed in the dark after a week, is effected in ten minutes in daylight. Benzyl bromide is formed in this case, together with small quantities of more highly brominated derivatives. Pure benzyl bromide is obtained by dropping bromine into eight times its weight of toluene kept at 80°. P. H.

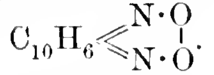
Preparation of Aromatic Sulphonamates by Reduction of Nitro-derivatives with Sodium Hyposulphite. Alphonse Seyewetz and Bloch (*Compt. rend.*, 1906, **142**, 1052—1054).—A mixture of nitrobenzene (63 grams), trisodium phosphate (75 grams), and sodium hyposulphite (380 grams) is made, and to it a litre of boiled water is added, and the whole vigorously shaken for some minutes and then set aside. After twenty-four hours, a quantity of sodium phenylsulphonamate will have separated; a second fraction may be obtained by cooling the mother liquor to 0°, and a third by then evaporating the mother liquor to dryness and extracting the residue with alcohol. The yield of the sodium salt is about equal to that of the nitrobenzene taken. The process is also applicable to the preparation of the corresponding sulphonamates from the three nitrotoluenes, *m*-nitro-xylene, and *α*-nitronaphthalene. T. A. H.

Additive Compounds of Aromatic Hydrocarbons with Polynitro-derivatives.

Giuseppe Bruni and L. Ferrari (*Chem. Zeit.*, 1906, **30**, 568—569).—The authors have prepared additive compounds of diphenyl, diphenylmethane, triphenylmethane, dibenzyl, stilbene, tolane, and azobenzene with picryl chloride, and find that the number of molecules of the latter compound which combines with one molecule of the hydrocarbon is proportional to the number of benzene rings contained in the hydrocarbon. P. H.

Constitutional Formula of 1 : 2-Dinitrosonaphthalene.

Giacomo Ponzio (*Atti R. Accad. Sci. Torino*, 1906, **41**, 588—591).—Contrary to the statement of Koreff (Abstr., 1886, 363), 1 : 2-dinitrosonaphthalene can be reduced by means of tin and hydrochloric acid, yielding naphthafurazan (Goldschmidt and Schmidt, Abstr., 1884, 1359) and 1 : 2-naphthylenediamine. The author hence regards 1 : 2-dinitrosonaphthalene as *β*-naphthaquinonedioxime peroxide,



$C_{10}H_6\Big<\begin{matrix}N\cdot O\\ \quad|\\ N\cdot O\end{matrix}$.

Oxidation of this compound in concentrated sulphuric acid solution by means of nitric acid of sp. gr. 1·52 yields the *dinitro*-derivative, $C_{10}H_4(NO_2)_2{:}N_2O_2$, which crystallises from acetic acid in yellow prisms melting at 212°, is moderately soluble in ethyl acetate or nitric acid, and dissolves in alkali solution, giving a red coloration.

T. H. P.

Synthesis of Alkyl Derivatives of 2 : 4-Dinitroaniline and of Two *iso*Propyl-2 : 4 : 6-Trinitroanilines.

A. Mulder (*Rec. trav. chim.*, 1906, **25**, 108—116).—The author prepared a number of these alkyl derivatives by Clemm's method (*J. pr Chem.*, 1869, **108**, 320, and 1870, ii, **1**, 170), which consists in treating 1-bromo-2 : 4-dinitrobenzene with the appropriate amine. Negative results, however, were obtained with di*iso*propylamine and ethyl*iso*propylamine, due probably to the influence of the secondary carbon atom in the *iso*propyl groups.

2 : 4-*Dinitromethylpropylaniline*, $C_6H_3(NO_2)_2NPr^aMe$, obtained by the action of methylpropylamine on the bromodinitrobenzene, forms bright yellow, prismatic crystals, melts at 71—72°, and is readily soluble in acetone or warm alcohol. 2 : 4-*Dinitroethylpropylaniline*, prepared similarly, separates from methyl alcohol in small, flattened, prismatic, yellow crystals and melts at 54—55°. 2 : 4-*Dinitrophenylbenzylmethylamine* crystallises from hot alcohol in bright yellow spangles, melts at 143—144°, and is readily soluble in benzene, acetone, or warm alcohol, less so in chloroform or ether. 2 : 4-Dinitrophenylbenzylethylamine separates from ether in large, bright yellow, transparent crystals and melts at 72—73° (compare Schultz, Rohde,

and Bosch, Abstr., 1904, i, 992). 2:4-*Dinitrophenylbenzylamine* separates from a mixture of acetone and alcohol in small, bright yellow, prismatic crystals and melts at 115—116°. 2:4-Dinitrophenyldibenzylamine melts at 104—105° (compare Pinnow and Wiskott, Abstr., 1899, i, 501). 2:4-Dinitrophenylethylaniline melts at 95° (compare Deletra and Ullmann, Abstr., 1904, i, 272). 2:4-*Dinitrophenylbenzylaniline*, obtained by heating in a closed vessel at 100°, a mixture of 1-bromo-2:4-dinitrobenzene, benzylaniline, and sodium acetate in presence of alcohol, forms small, red crystals from warm acetone and melts at 168°.

2:4-*Dinitrophenylpropylaniline* is best prepared by heating propylaniline, obtained by Pictet and Crepieux's method (Abstr., 1888, i, 688), with bromodinitrobenzene, dissolved in alcohol, under pressure. It crystallises in brown spangles with a green sheen or in small needles of the same tint, and melts at 73—74°.

When di*iso*propylamine reacts with bromodinitrobenzene dissolved in alcohol, four products are formed: (1) bright yellow needles melting at 81°, (2) orange prisms melting at 106—107°, (3) prisms resembling those of No. 2, but melting at 89—90°, and (4) yellow spangles melting at 123°. None of these substances can be the 2:4-dinitrodi*iso*propylaniline expected.

Ethyl *iso*propylamine reacts very slowly with an alcoholic solution of bromodinitrobenzene, yielding an oil from which no well-defined amine can be isolated. When this oil is treated with picryl chloride, it furnishes 2:4:6-*trinitroethyl*iso*propylaniline*, which exists in two forms: (1) red needles, and (2) yellow spangles. The first form passes into the second at 90°, and the latter melts at 108—109°.

2:4-*Dinitro*iso*propylaniline* crystallises in large, flattened, yellow needles from acetone, and in spangles from warm alcohol, and melts at 94—95°. When added to warm nitric acid of sp. gr. 1·52 and the solution boiled, this substance is converted into van Romburgh's 2:4:6-trinitrophenyl*iso*propylnitroamine, which melts at 107° (compare Abstr., 1886, i, 455).

2:4:6-*Trinitro*iso*propylaniline* crystallises from a mixture of alcohol and acetic acid in yellow needles and melts at 106—107°.

T. A. H.

Oxidation of 2:4-Dinitroanilines with Chromic Anhydride. A. Mulder (*Rec. trav. chim.*, 1906, 25, 117—120).—Van Romburgh has shown that when 2:4-dinitrodialkylanilines, dissolved in acetic acid, are oxidised with chromic acid, the alkyl groups are successively replaced by hydrogen atoms, and that when two different alkyl groups are present only one of the two possible dinitroalkylanilines is formed (Abstr., 1889, 971; 1896, i, 478). The author oxidised several of the 2:4-dinitrodialkylanilines described in the preceding abstract by van Romburgh's method and found that in most cases in addition to dinitroaniline both possible dinitromonoalkylanilines were produced, although usually one was formed in much larger quantity than the other.

2:4-Dinitrophenyldibenzylamine, on oxidation by chromic acid in presence of acetic acid, yielded 2:4-dinitrophenylbenzylamine in addition to dinitroaniline, and not the latter only, as Pinnow and Wiskott assert (Abstr., 1899, i, 500). T. A. H.

Hexanitrodiphenylamines. A. Mulder (*Rec. trav. chim.*, 1906, **25**, 121—123).—When 2 : 4-dinitrophenylmethylaniline is added to nitric acid of sp. gr. 1·49, and, after the first violent action has subsided, the solution is heated to the boiling point for fifteen minutes, *hexanitrodiphenylmethylamine* is formed. This crystallises from acetic acid in small, yellow spangles and melts at 236—237°, and when boiled with an aqueous solution of potassium hydroxide yields methylamine. *Hexanitrodiphenylethylamine*, obtained in a similar manner, forms small, colourless needles, becomes brown on exposure to light, and melts at 198—200°. It yields ethylamine when boiled with an aqueous solution of potassium hydroxide, but is resistant to chromic acid, yielding, with the latter, only a small quantity of resinous products *Hexanitrodiphenylpropylamine* forms small, bright yellow needles and melts at 136—137°. These three substances all give intense red colorations with alkalis. T. A. H.

Hydrogen Phosphites of Primary Cyclic Amines. Paul Lemoult (*Compt. rend.*, 1906, **142**, 1193—1195).—When phosphorus trichloride (1 mol.) and aniline (6 mols.) are mixed in ethereal solution, aniline hydrochloride is precipitated, and the resulting mother liquor slowly absorbs water from the air and deposits voluminous white crystals of the acid phosphite of the base; the same product is obtained if chloroform is used as a solvent instead of ether, and the hydration is hastened by warming the solution at 100°. The hydrogen phosphites of the primary cyclic amines are insoluble in ether, chloroform, or benzene, but can be recrystallised from alcohol; they have definite melting points, but decompose at a slightly higher temperature with the formation of the primary base, hydrogen phosphide, and ortho-phosphoric acid. *Hydrogen aniline phosphite*, $C_6H_5\cdot NH_2,H_3PO_3$, forms beautiful pale red or green needles, or large, brilliant crystals which melt at 179°, and is precipitated by alcohol from aqueous solution in the form of small plates melting at 179°. *Hydrogen* o-*toluidine phosphite*, $C_7H_7\cdot NH_2,H_3PO_3$, forms beautiful, colourless needles which melt at 174° and decompose at 200°. *Hydrogen* as-m-*xylidine phosphite*, $C_8H_9\cdot NH_2,H_3PO_4$, crystallises in colourless needles and melts at 172°. M. A. W.

Formation of Salts of Aromatic Bases with Dicarboxylic Acids. Otto Anselmino (*Chem. Centr.*, 1906, i, 753; from *Ber. Deut. pharm. Ges.*, **15**, 422—426. Compare Abstr., 1904, i, 306).—The results of experiments on the behaviour of oxalic and succinic acids towards a further series of aromatic bases have not indicated any regularity either in reference to the possibility of the formation of salts or to the stability of the salts. *o*-Anisidine and *m*-nitroaniline form acid oxalates; *as-m*-xylidine and *o*- and *m*-aminobenzoic acids, normal oxalates and aniline, *o*-, *m*-, and *p*-toluidines, *p*-anisidine, *p*-phenetidine, *ψ*-cumidine, *p*-aminobenzoic acid. and *α*- and *β*-naphthylamines yield both acid and normal oxalates. The acid reaction of the acid oxalates of *m*- and *p*-toluidines is not affected by boiling with alcohol, but the acid oxalates of aniline, *o*-toluidine, *p*-anisidine, *p*-phenetidine, *p*-aminobenzoic acid, and of α- and β-naphthylamines become neutral; the acid oxalates of *o*-toluidine, *o*-anisidine, *o*-aminobenzoic acid, *m*- and *p*-nitroaniline, and of α- and β-naphthylamine form condensation products.

Aniline, *o*- and *p*-toluidine, *o*- and *p*-anisidine, *as*-*m*-xylidine, and β-naphthylamine form acid succinates.

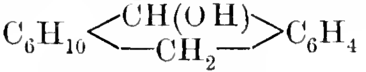
o-*Toluidine oxalate* melts at 167°, o-*toluidine hydrogen oxalate* at 171°, as-m-*xylidine oxalate* at 167°, ψ-*cumidine oxalate* at 183°, ψ-*cumidine hydrogen oxalate* at 179°, m-*aminobenzoic acid oxalate* at 246°, p-*aminobenzoic acid hydrogen oxalate* above 275°, p-*aminobenzoic acid oxalate* above 275°, p-*phenetidine oxalate* at 201°, p-*phenetidine hydrogen oxalate* at 201°, β-*naphthylamine oxalate* at 181°, and β-*naphthylamine hydrogen oxalate* at 176°.

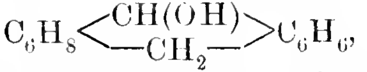
o-*Toluidine oxalo*-o-*toluidate*, $C_{16}H_{18}O_3N_2$, melts at 153°; *oxalo*-o-*anisic acid*, $C_9H_9O_4N$, at 159°; m-*nitro-oxanilic acid*, $C_8H_6O_5N_2$, at 158°, and *ethyl* p-*nitro-oxanilate*, $C_{10}H_{10}O_5N_2$, at 168°. β-*Naphthylamine* β-*naphthyloxamate*, $C_{22}H_{22}O_3N_2$, is also a condensation product.

E. W. W.

Influence of Catalysts on the Formation of Anilides. II. Nicolai A. Menschutkin (*Chem. Centr.*, 1906, i, 551; from *Iswiestja Petersburg Polytechn. Inst.*, 1905, 4, 181—190. Compare Abstr., 1903, i, 813).—The accelerating influence of hydrogen chloride, bromide, or iodide on the rate of acetylation of aniline, *o*-, *m*-, or *p*-toluidine, and *m*- or *p*-xylidine by acetic acid was found to be proportional to the molecular weight of the acid and to the quantity employed. In the presence of these acids, the reaction was uni-molecular, otherwise it was bi-molecular. A methyl group in the ortho-position decreases the velocity of acetylation, whereas in the meta- or para positions it increases it.

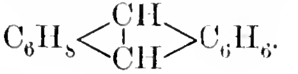
P. H.

Some Hydroanthracene Derivatives. Marcel Godchot (*Compt. rend.*, 1906, 142, 1202—1204. Compare Abstr., 1904, i, 987; 1905, i 201).—*Octahydroanthranol*,  $C_6H_{10}{<}\begin{matrix}CH(OH)\\CH_2\end{matrix}{>}C_6H_4$ or


$C_6H_8{<}\begin{matrix}CH(OH)\\CH_2\end{matrix}{>}C_6H_6$,

obtained by reducing hexahydroanthrone by means of sodium and alcohol, crystallises in small, yellow needles, melts at 81—82°, is very soluble in the ordinary solvents, and loses H_2O on distillation even in a vacuum to form a hexahydroanthracene; the *phenylurethane*, $C_{14}H_{17}O{\cdot}CO{\cdot}NHPh$, crystallises from acetone in beautiful, colourless needles which melt at 151—152°.

β-*Hexahydroanthracene*, isomeric with the compound described by Graebe and Liebermann (Abstr., 1882, 857), obtained from octahydroanthranol either by distillation or by boiling it in alcoholic solution with a few drops of hydrochloric acid, or by heating it with acetic or benzoic anhydride or chloride, crystallises in small, colourless plates;

it melts at 66·5°, boils at 303—306°, is insoluble in water, soluble in hot alcohol, acetic acid or benzene, the solutions exhibiting a beautiful blue fluorescence. It yields dihydro-oxanthranol on oxidation, and reacts with chlorine or bromine to form dichloro- or dibromo-octahydroanthracene identical with the compounds similarly obtained from octahydroanthracene (Abstr., 1904, i, 987); β-hexahydroanthracene has therefore the formula  $C_6H_{10}<\overset{CH}{\underset{CH}{|}}>C_6H_4$ or  $C_6H_8<\overset{CH}{\underset{CH}{|}}>C_6H_6$.

9 : 10-*Tetrahydroanthracene*,  $C_6H_6<\overset{CH_2}{\underset{CH_2}{}}>C_6H_4$, obtained by reducing dihydro-oxanthranol by means of hydrogen iodide, forms colourless plates which melt at 101°, is readily soluble in the ordinary reagents, and the solutions are not fluorescent; it yields dihydro-oxanthranol on oxidation, and readily forms substitution products with chlorine or bromine. 9 : 10-*Dibromotetrahydroanthracene*,  $C_6H_6<\overset{CHBr}{\underset{CHBr}{}}>C_6H_4$, crystallises in large, yellow needles, melts at 169°, and is not attacked by aqueous or alcoholic potassium hydroxide at 250°.

M. A. W.

Phenol. Hugo Kühl (*Chem. Centr.*, 1906, i, 344—345; from *Pharm. Zeit.*, **50**, 1001).—When phenol which has been kept for a long time and has become red is distilled, a solid, violet-red residue remains, which is insoluble in water or ammonia. By the action of hydrogen peroxide on an ammoniacal solution of phenol, a green coloration is formed after some time. No characteristic coloration is formed when sodium nitrite is added to a solution of phenol in concentrated sulphuric acid. When heated with a solution of ferric chloride and evaporated on the water-bath, a residue is left which has a faint red tinge.

E. W. W.

Aluminium Phenoxide. Alfred N. Cook (*J. Amer. Chem. Soc.*, 1906, **28**, 608—617).—A method is described for the preparation of aluminium phenoxide, $Al(OPh)_3$ (Gladstone and Tribe, Trans., 1882, **41**, 5). The compound is a grey, translucent, brittle solid which melts at 265°, has a vitreous lustre, a sp. gr. 1·23, and is soluble in hot benzene, toluene, or xylene, and also in dry alcohol, chloroform, carbon disulphide, or acetone. The compound is decomposed by water with formation of aluminium hydroxide. It reacts with bromine with production of tribromophenol bromide. When aluminium phenoxide is treated with nitric acid, *o*-nitrophenol, 1 : 2 : 4-dinitrophenol, and picric acid are produced. The substance reacts with alcohol with formation of aluminium ethoxide and phenol, and also with ether with production of aluminium ethoxide and phenetole. The action of several other reagents is described. Aluminium phenoxide is decomposed by heat with formation of benzene, phenol, phenyl ether, and some higher boiling substances which have not been identified. This decomposition affords a good method for the preparation of phenyl ether.

E. G.

5-Nitro-2-aminophenol. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 165650).—5-Nitro-2-aminophenol is readily obtained by dissolving ethenyl-*o*-aminophenol in cold concentrated sulphuric acid and nitrating with a mixture of this acid and nitric acid. The nitroethyl-*o*-aminophenol thus produced is boiled with an equal weight of hydrochloric acid until solution is complete, when 5-nitro-2-aminophenol is precipitated on neutralising the solution with sodium or calcium carbonate. G. T. M.

Action of Benzyl Chloride on Aminophenols MARUSSIA BAKUNIN (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1905, [iii], **11**, 361—375).—When *p*-aminophenol and benzyl chloride are heated together in alcoholic solution in presence of zinc, an organo-zinc chloro-compound melting at 240° is obtained, which, on decomposition with water, gives rise to benzylaminophenol hydrochloride melting at 224°.

The interaction of *p*-aminophenol and benzyl chloride in alcoholic solution yields: (1) p-*dibenzylaminophenol hydrochloride*,

$$OH\cdot C_6H_4\cdot NHCl(CH_2Ph)_2,$$

which crystallises from alcohol in short, colourless, monoclinic prisms melting at 200—224°, and is almost insoluble in the ordinary organic solvents; water dissolves it and liberates the free base, a decomposition more readily effected by dilute sodium hydroxide or carbonate solution, or by the action of metallic zinc on the alcoholic solution. (2) A small quantity of p-*benzylaminophenol hydrochloride*,

$$OH\cdot C_6H_4\cdot NH_2Cl\cdot CH_2Ph,$$

which crystallises from water in long, glassy prisms containing H_2O, and melts in its water of crystallisation at 130° and afterwards at 172°; it is soluble in alcohol or acetic acid. The free *base*,

$$OH\cdot C_6H_4\cdot NH\cdot CH_2Ph,$$

separates from alcohol or water in nacreous laminæ melting at 89—90° and dissolves in benzene or chloroform.

The interaction of *o*-aminophenol and benzyl chloride yields: (1) o-*dibenzylaminophenol hydrochloride*, $C_{20}H_{19}ON,HCl$, which crystallises from water or alcohol in regular octahedra melting at 200—205°; (2) *o*-benzylaminophenol hydrochloride; the free *base* crystallises from light petroleum in nacreous laminæ melting at 81—82°. T. H. P.

Action of Iodine Chloride on Catechol. C. LORING JACKSON and M. C. BOSWELL (*Amer. Chem. J.*, 1906, **35**, 519—531).—The experiments described were carried out with the object of preparing tetraiodo-*o*-benzoquinone.

By the action of iodine chloride (270 grams) on catechol (30 grams), a dark red mass is produced containing a large quantity of iodine. On removing the iodine by means of potassium iodide solution, a substance, probably *octachlorotri-iodopentacatechol*, $C_{20}H_{19}O_{10}Cl_8I_3$, is obtained, which crystallises from dilute alcohol in long, white, silky needles, melts at 224°, and is soluble in ether, benzene, or acetic acid; its *diacetyl* derivative was prepared. This compound is converted by nitric acid into a dark red *substance*, which crystallises from toluene in long, bright red needles, becomes darker on drying, owing probably to loss of toluene of crystallisation, and then melts at 272°; it tends to become light yellow when treated with benzene, light petroleum, or dilute acetic acid.

If the iodine is not removed from the product of the reaction before treatment with sulphur dioxide, trichlorocatechol is produced, which crystallises with H_2O and melts at 115° instead of 104—105°, as stated by Cousin (Abstr., 1895, i, 456).

If 30 grams of catechol are treated with 360 grams of iodine chloride, a compound is obtained, probably *heptachloroiodotricatechol*, $C_{18}H_{10}O_6Cl_7I$, which crystallises from hot dilute alcohol in long, white, silky needles, melts at 252°, and is soluble in alcohol or acetic acid; its *diacetyl* derivative was prepared.

If in preparing this compound the reduction with sulphur dioxide is effected before removing the iodine, tetrachlorocatechol (m. p. 194—195°) is produced, which crystallises with H_2O.

Indications have been obtained that by varying the proportion of iodine chloride another compound may be obtained which melts at 270°.

Attempts were made by other methods to prepare tetraiodocatechol or tetraiodo-*o*-quinone, but without success. E. G.

Phloroglucinol. MAXIMILIAN NIERENSTEIN (*Chem. Centr.*, 1906, i, 553; from *Collegium*, 1906, 14—15).—Phloroglucinol, when treated in ethereal solution with diazomethane, gives an almost quantitative yield of an enolic ether melting at 52·5°, and it is therefore suggested that diazomethane might be a useful reagent for the study of tautomeric modifications. Both resorcinol and pyrogallol give the pine shaving reaction which hitherto has been supposed to be characteristic of phloroglucinol. P. H.

Preparation of Dialkylmalonyl-*p*-phenetidines. AKTIENGESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 165311).—Dialkylated malonylphenetidines are obtained by the interaction of 2 mols. of phenetidine and 1 mol. of dialkylmalonyl chloride, the former reagent being dissolved in benzene. Clinical experiments have shown that in addition to their antipyretic properties these dialkylmalonyl-*p*-phenetidines have also a saporific action.

Diethylmalonyl-p-*phenetidine*, $CEt_2(CO\cdot NH\cdot C_6H_4\cdot OEt)_2$, crystallises from alcohol in white needles melting at 186°; it is sparingly soluble in hot water, but dissolves readily in hot alcohol or benzene.

Dipropylmalonyl-p-*phenetidine*, $CPr^{\alpha}_2(CO\cdot NH\cdot C_6H_4\cdot OEt)_2$, resembles the preceding compound and melts at 143°. G. T. M.

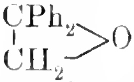
Preparation of Aromatic Alcohols and their Ethers by the Electrolytic Reduction of Aromatic Esters. CARL METTLER (D.R.-P. 166181).—The carboxyl group of an aromatic ester can be reduced electrolytically when the metal chosen for cathode has a high supertension, lead being the best metal for the purpose. It is necessary also to have a solvent which can conduct the electric current, and concentrated sulphuric acid is found convenient since it may be diluted with water, alcohol, or glacial acetic acid; this solvent may, however, be replaced by an aqueous-alcoholic solution of phosphoric or hydrochloric acid. Under these conditions the alkyl esters of benzoic acid and its derivatives are reduced, yielding a mixture of the corresponding alcohol and its alkyl ether; the proportion of the two products depends on the constitution of the original ester. In alkaline solutions the alcohol alone is produced. These alcohols and their ethers are readily oxidised to the technically important aromatic aldehydes.

Ethyl benzoate when electrolysed in the cathode cell with a current density of 7 amperes per 100 sq. cm at 20—30° yielded a mixture of benzyl alcohol and benzyl ethyl ether; the solvent in this case was a mixture of dilute sulphuric acid and alcohol. With this solvent and at a temperature of 60—80°, phenyl benzoate gave rise to a mixture of benzyl alcohol and phenyl benzyl ether. Ethyl *m*-bromobenzoate furnished *m*-bromobenzyl ethyl ether and a small amount of *m*-bromobenzyl alcohol. Benzyl benzoate yielded benzyl alcohol and dibenzyl ether.

In presence of aqueous-alcoholic ammonia, ethyl benzoate on electrolysis furnished only benzyl alcohol. G. T. M.

Benzyl *iso*Valerate. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 165897).—*Benzyl* iso*valerate*, $CHMe_2 \cdot CH_2 \cdot CO_2 \cdot CH_2Ph$, is an ester having valuable therapeutic properties, being a sedative which has no harmful effect on the mucous membrane of the stomach. It is prepared by heating together benzyl chloride and sodium *iso*valerate for ten hours at 160° and purified by fractionation under diminished pressure. The ester which has a pleasant odour and boils at 136° under 25 mm. pressure, can also be prepared by the following processes: the interaction of benzyl alcohol and *iso*valeryl chloride either in pyridine-benzene solution or in the presence of concentrated sulphuric or hydrochloric acid; the condensation of benzyl alcohol and carbonyl chloride in quinoline solution and the interaction of the resulting benzyl chlorocarbonate with sodium *iso*valerate at 160°; the direct condensation of *iso*valeric anhydride and benzyl alcohol at 180—200°. G. T. M.

Unsymmetrical Diphenylethylene Oxide. AUGUST KLAGES and JOHANNES KESSLER (*Ber.*, 1906, **39**, 1753—1756. Compare Abstr., 1905, i, 523; Tiffeneau and Fourneau, Abstr., 1905, i, 523, 591; this vol., i, 20).—as-*Diphenylchlorohydrin* [*diphenylchloromethyl carbinol*], $OH \cdot CPh_2 \cdot CH_2Cl$, obtained by the interaction of magnesium phenyl bromide (3 mols.) and ethyl chloroacetate (1 mol.) with subsequent decomposition of the product by cold water, melts at 66°, and its vapour has an irritating action on the eyes. It reacts with diethylamine at 100° to give a poor yield of *diphenyldiethylaminomethylcarbinol*, $NEt_2 \cdot CH_2 \cdot CPh_2 \cdot OH$, which melts at 49°, and a *substance* which melts at 154—155° and does not contain nitrogen.

as-*Diphenylethylene oxide*,  $\left.\begin{array}{l}CPh_2\\ \vert\\ CH_2\end{array}\right>O$, obtained from the chlorohydrin and sodium ethoxide, is a colourless substance which melts at 56°, turns yellow in the air, and slowly becomes resinous; its vapour has a pungent odour and is volatile in steam. The sodium hydrogen sulphite compound is decomposed by boiling dilute sulphuric acid or potassium carbonate with the formation of diphenylacetaldehyde, of which the *semicarbazone* melts at 160°, the *azine* at 165°, and the *benzoylhydrazone* at 182°. C. S.

Further Investigations of the Two Chlorides of *o*-Sulphobenzoic Acid. PHILIP H. COBB (*Amer. Chem. J.*, 1906, **35**, 486—508).—Experiments on the action of hydrochloric acid on organic anhydrides have led to the conclusion that the formation of symmetrical ester chlorides by the action of alcohol on the more fusible chloride of *o*-sulphobenzoic acid is not dependent on the presence of hydrochloric acid. It has been found that the anhydrides of certain dibasic acids do not react with dry hydrogen chloride, whilst those of monobasic acids are easily attacked.

The action of alcohols and alkyloxides on the chlorides has been studied by Bird (Abstr., 1903, i, 822). The product obtained by the action of methyl alcohol on the more fusible chloride melts at 63—64°. The barium salt containing about 28 per cent. of barium which was obtained by Bird from the product formed by boiling either the less fusible or more fusible chloride with 95 per cent. ethyl alcohol is probably a mixture of salts of *o*-sulphobenzoic acid and the ester acid. Sodium ethoxide reacts with both chlorides with formation of diethyl *o*-sulphobenzoate in each case.

By the action of benzene on the chlorides in presence of aluminium chloride, Remsen and Saunders (Abstr., 1895, i, 474) and List and Stein (Abstr., 1898, i, 584) obtained *o*-benzoyldiphenylsulphone together with a product which melts at 162—163° and was regarded as the lactone,  $C_6H_4<{CPh_2 \atop SO_2}>O$. It is now considered probable that this product is not the supposed lactone.

By the action of thionyl chloride on dipotassium *o*-sulphobenzoate, *o*-sulphobenzoic anhydride is obtained together with a small quantity of the salt, $COCl\cdot C_6H_4\cdot SO_3K$, but no *o*-sulphobenzoic chloride could be isolated. By the action of thionyl chloride on the acid potassium salt, the anhydride can be obtained in an 80 per cent. yield.

When the anhydride is heated with phosphorus oxychloride at 125° for fourteen hours, the more fusible chloride is produced.

By the action of magnesium phenyl bromide on the less fusible chloride, the *substance* $SO_2Ph\cdot C_6H_4\cdot CPh_2\cdot OH$ is obtained, which crystallises from alcohol, melts at 183—184°, and gives a dark red coloration with concentrated nitric and sulphuric acids. The same substance can be obtained by treating *o*-benzoyldiphenylsulphone with magnesium phenyl bromide. Magnesium phenyl bromide reacts with *o*-sulphobenzoic anhydride with formation of the compound melting at 163°, which is obtained by the action of benzene on the less fusible chloride in presence of aluminium chloride. E. G.

Preparation of Methylenehippuric Acid. CHEMISCHE FABRIK AUF AKTIEN VORM. E. SCHERING (D.R.-P. 163238. Compare Abstr., 1904, i, 413).—Hippuric acid reacts with chloromethyl alcohol or the less volatile fractions containing hydroxymethylene chlorides (Litterscheid, Abstr., 1901, i, 443) to form methylenehippuric acid. There is less formation of resin than when formaldehyde and an acid are employed. C. H. D.

[Crystallographic Measurements of] Derivatives of Phenylcarbamic Acid. F. M. Jaeger (*Zeit. Kryst. Min.*, 1906, **42**, 25—33).—Methyl phenylcarbamate crystallises from alcohol in colourless, rectangular leaflets which melt at 47° and belong to the bipyramidal class of the rhombic system $[a:b=1{\cdot}5952:1]$; it has a sp. gr. 1·251 at 19°.

Methyl phenylmethylcarbamate separates from alcohol in large, colourless crystals which melt at 44° and belong to the bipyramidal class of the rhombic system $[a:b:c=0{\cdot}8406:1:0{\cdot}3320]$; sp. gr. 1·296 at 19°.

Methyl 4-nitrophenylmethylcarbamate separates from alcohol or benzene in fine needles or large, pale yellow, somewhat flattened crystals which melt at 108° and belong to the prismatic class of the monoclinic system $[a:b=0{\cdot}6640:1;\ \beta=70^\circ58']$; sp. gr. 1·522 at 14°.

Methyl 2 : 4-dinitrophenylmethylcarbamate crystallises from xylene in pale yellow, parallelogramatic plates, which melt at 98° and belong to the prismatic class of the monoclinic system

$$[a:b:c=0{\cdot}7597:1:1{\cdot}0875;\ \beta=88^\circ43\tfrac{1}{3}'];$$

sp. gr. is 1·506 at 14°.

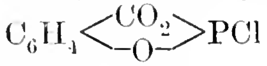
Methyl 2 : 4 : 6-trinitrophenylcarbamate melts at 118° and is dimorphous. The α-modification is the one usually separating from solvents and is deposited from acetone in very shiny, colourless or pale yellow crystals belonging to the prismatic class of the monoclinic system $[a:b:c=0{\cdot}5758:1:0{\cdot}8382;\ \beta=75^\circ41']$; sp. gr. 1·612 at 19°. The β-modification occasionally separates from alcohol, along with the α-form, in long, orange needles which turn yellow at about 105° and melt somewhat below 118°; these crystals belong to the bipyramidal division of the rhombic system $[a:b=0{\cdot}6596:1]$; sp. gr. at 19° is 1·601.

Ethyl 2 : 4-dinitrophenylmethylcarbamate is deposited from a mixture of benzene and light petroleum in large, colourless, shining crystals, which melt at 112° and belong to the prismatic division of the monoclinic system $[a:b:c=0{\cdot}6525:1:0{\cdot}7035;\ \beta=69^\circ59']$; sp. gr. 1·461 at 19°.

Ethyl 2 : 4 : 6-trinitrophenylmethylcarbamate crystallises from a mixture of benzene and light petroleum in slender, transparent, pale yellow needles, which melt at 65° and belong to the prismatic division of the monoclinic system $[a:b:c=0{\cdot}9759:1:0{\cdot}3929;\ \beta=67^\circ7']$; sp. gr. at 14°, 1·471.

2 : 4 : 6-Trinitrophenylnitromethylamine crystallises from a mixture of benzene and acetone in small, highly refractive, pale yellow needles, which melt at 127° and belong to the prismatic class of the monoclinic system $[a:b:c=2{\cdot}7823:1:3{\cdot}5242;\ \beta=75^\circ31\tfrac{1}{2}']$; sp. gr. at 19°, 1·570. T. H. P.

Action of Phosphorus Pentachloride and Trichloride on Substituted *o*-Phenolcarboxylic Acids. Richard Anschütz (*Annalen*, 1906, **346**, 286—300. Compare Anschütz and Emery, Abstr., 1887, 946; Anschütz and Moore, Abstr., 1887, 947; Couper, *Compt. rend.*, 1858, **46**, 1107).—The author discusses the constitution of salicylphosphorous chloride formed by the action of phosphorus trichloride, and of chlorocarboxyphenyl dichloro-orthophosphate formed by the action of phosphorus pentachloride on salicylic acid, and concludes that they must be represented by the formulæ



$$C_6H_4<\begin{matrix}CO_2\\O\end{matrix}>PCl$$

and $COCl{\cdot}C_6H_4{\cdot}O{\cdot}POCl_2$ respectively.

Chlorocarboxyphenyl dichloro-orthophosphate, prepared by the action of phosphorus pentachloride on salicylic acid, is identical with the products of the action of chlorine and of phosphorus pentachloride on salicylphosphorous chloride, as when heated with anhydrous oxalic acid at 75—85° all three preparations yield *o*-chlorocarboxyphenyl metaphosphate (Anschütz and Moore, *loc. cit.*), which crystallises from a mixture of benzene and light petroleum, melts at 95°, and boils at 170—171° under 11 mm. pressure.

The *additive* compound, formed by the action of bromine on salicylphosphorous chloride, distils at 185—190° and is a mixture of the compounds $COBr{\cdot}C_6H_4{\cdot}O{\cdot}POClBr$ and $COCl{\cdot}C_6H_4{\cdot}O{\cdot}POBr_2$, as when heated with anhydrous oxalic acid at 85—100° it yields hydrogen chloride and bromide, carbon monoxide and dioxide, and an almost molecular *mixture* of the compounds $C_7H_4O_4ClP$ and $C_7H_4O_4BrP$, which melts at 96—98° and boils at 205—210°, or after repeated distillation at 178—182° under 11 mm. pressure. G. Y.

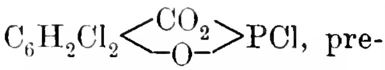
Action of Phosphorus Pentachloride and Trichloride on 3 : 5-Dichlorosalicylic Acid. RICHARD ANSCHÜTZ and HEINRICH MEHRING (*Annalen*, 1906, **346**, 300—311. Compare preceding abstract).—3 : 5-Dichlorosalicylic acid forms transparent, rhombic crystals [$a : b : c = 0{\cdot}9983 : 1 : 1{\cdot}2312$] and melts at 219° (214° : Smith, Abstr., 1878, 879). The *chloride*, $OH{\cdot}C_6H_2Cl_2{\cdot}COCl$, formed by heating the acid with 1 mol. of phosphorus pentachloride at 60°, crystallises from a mixture of ether and light petroleum, melts at 79°, and is hydrolysed slowly by moist air, quickly by hot water. The methyl ester, which melts at 147° (143° : Smith, *loc. cit.*) and boils at 160°, and the ethyl ester, which forms rhombic crystals [$a : b : c = 0{\cdot}9403 : 1 : 0{\cdot}4273$], melts at 57° (47° : Smith, *loc. cit.*) and boils at 159° under 11·5 mm. pressure, are prepared by the action of methyl and ethyl alcohols respectively on the acid chloride. The *phenyl ester*, $OH{\cdot}C_6H_2Cl_2{\cdot}CO_2Ph$, crystallises in transparent, rhombic plates [$a : b : c = 0{\cdot}72877 : 1 : ?$], melts at 118·5°, and decomposes at 139° under 14 mm. pressure, forming phenol and poly-3 : 5-dichlorosalicylide. The *anilide*, $OH{\cdot}C_6H_2Cl_2{\cdot}CO{\cdot}NHPh$, forms sheaves of transparent crystals, which effloresce when exposed to air, and melts at 134·5°. The *piperidide*, $OH{\cdot}C_6H_2Cl_2{\cdot}CO{\cdot}C_5H_{10}N$, crystallises in asymmetric plates [$a : b : c = 0{\cdot}6707 : 1 : 0{\cdot}660$] and melts at 108°. The *anhydride*, $O(CO{\cdot}C_6H_2Cl_2{\cdot}OH)_2$, formed by boiling the acid chloride with the silver salt suspended in ether, crystallises from chloroform, melts at 186—187°, and is only sparingly soluble in water. The *silver*, $C_7H_3O_3Cl_2Ag$, and *ammonium*, $C_7H_7O_3NCl_2$, salts were analysed.

4 : 6-*Dichloro-2-trichloromethylphenyl dichloro-orthophosphate*,

$$CCl_3{\cdot}C_6H_2Cl_2{\cdot}O{\cdot}POCl_2,$$

is prepared by heating 3 : 5-dichlorosalicylic chloride with 1 mol. of phosphorus pentachloride in a sealed tube at 50—60° for twelve hours; it separates from acetone in transparent crystals, which become opaque on exposure to air, melts at 102—104°, is hydrolysed to 3 : 5 dichlorosalicylic acid when boiled with water for some hours, and, when heated with 1 mol. of phosphorus pentachloride in a sealed tube at 200° yields a mixture of products boiling at 160—190° under 17 mm. pressure; of these, the main product is probably 2 : 3 : 5-trichlorobenzotrichloride.

Poly-3 : 5-dichlorosalicylide, $(O\cdot C_6H_2Cl_2\cdot CO)_x$, formed when phenyl 3 : 5-dichlorosalicylate or 3 : 5-dichlorosalicylic chloride is distilled under reduced pressure, separates from chloroform in white crystals, becomes blackish-brown at 250°, does not melt at 300°, and remains unaltered when boiled with water.

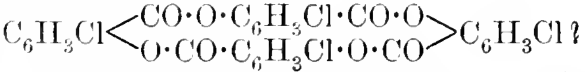
3 : 5-*Dichlorosalicylphosphorous chloride*,  $C_6H_2Cl_2\!\left<\begin{matrix}CO_2\\ O\end{matrix}\right>\!PCl$, prepared by boiling 3 : 5-dichlorosalicylic acid with phosphorus trichloride in xylene solution in a reflux apparatus, melts at 55°, boils at 159° under 11 mm. pressure, forms an *additive* compound with chlorine, and is hydrolysed readily by water, forming 3 : 5-dichlorosalicylic acid.

G. Y.

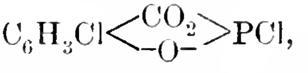
Action of Phosphorus Pentachloride and Trichloride on 3-Chlorosalicylic Acid.

Richard Anschütz and Richard Anspach (*Annalen*, 1906, **346**, 312—317. Compare preceding abstracts).—3-Chlorosalicylic acid melts at 180° (178°: Varnholt, Abstr., 1887, 945). 3-*Chlorosalicylic chloride*, $OH\cdot C_6H_3Cl\cdot COCl$, prepared by boiling the acid with phosphorus pentachloride in light petroleum solution in a reflux apparatus, crystallises in long, white needles, melts at 62—63°, and is readily soluble in ether, glacial acetic acid, benzene, chloroform, and carbon tetrachloride. The methyl ester, prepared by the action of methyl alcohol, melts at 38° (83°: Varnholt, *loc. cit.*); the *ethyl ester*, $OH\cdot C_6H_3Cl\cdot CO_2Et$, crystallises from alcohol in long, flat needles and melts at 21°, forming a strongly refractive oil with an aromatic odour, which boils at 147° under 12 mm. or at 269—270° under the ordinary pressure. The *anilide*, $OH\cdot C_6H_3Cl\cdot CO\cdot NHPh$, crystallises from alcohol in white, silvery needles and melts at 158·5—159°.

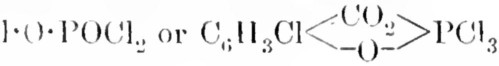
3-Chlorosalicylide and poly-3-chlorosalicylide are formed together with hydrogen chloride when 3-chlorosalicylic chloride is heated about 100° under greatly reduced pressure.

3-*Chlorosalicylide*,  $C_6H_3Cl\!\left<\begin{matrix}CO\cdot O\cdot C_6H_3Cl\cdot CO\cdot O\\ O\cdot CO\cdot C_6H_3Cl\cdot O\cdot CO\end{matrix}\right>\!C_6H_3Cl$? (compare Anschütz, Abstr., 1893, i, 165), is obtained as a white, voluminous powder, melts at 206°, and is readily soluble in chloroform.

Poly-3-chlorosalicylide, $(C_7H_3O_2Cl)_x$, separates from xylene as a hard crust, melts at about 330°, and is insoluble in chloroform.

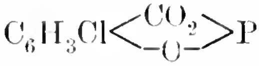
3-*Chlorosalicylphosphorous chloride*,  $C_6H_3Cl\!\left<\begin{matrix}CO_2\\ O\end{matrix}\right>\!PCl$, prepared by heating 3-chlorosalicylic acid with phosphorus trichloride in a reflux apparatus, melts at about 65°, boils at 150° under 12·5 mm.

pressure, and when heated with phosphorus pentachloride yields 6-*chloro-2-chlorocarboxyphenyl dichloro-orthophosphate*,

$COCl{\cdot}C_6H_3Cl{\cdot}O{\cdot}POCl_2$ or  $C_6H_3Cl<\substack{CO_2\\ -O-}>PCl_3$,

which boils at 195—196° under 13 mm. pressure and is readily hydrolysed by water. G. Y.

Action of Phosphorus Pentachloride and Trichloride on 5-Chlorosalicylic Acid.

RICHARD ANSCHÜTZ and RICHARD ANSPACH (*Annalen*, 1906, **346**, 318—323. Compare preceding abstracts).—5-*Chlorosalicylphosphorous chloride*,  $C_6H_3Cl<\substack{CO_2\\ -O-}>PCl$, formed by the action of phosphorus trichloride on 5-chlorosalicylic acid, melts at 55—57°, boils at 155—156° under 14 mm. pressure, is very sensitive to water, and when treated with phosphorus pentachloride at 105—115° yields 4-*chloro-2-chlorocarboxyphenyl dichloro-orthophosphate*,

$$COCl{\cdot}C_6H_3Cl{\cdot}O{\cdot}POCl_2,$$

which is formed also by the action of phosphorus pentachloride on 5-chlorosalicylic acid in light petroleum solution. It is obtained as a colourless, strongly refracting oil, which boils at 183—184° under 13 mm. pressure and is easily hydrolysed by moisture.

4-*Chloro-2-carboxyphenyl dihydrogen phosphate*,

$$CO_2H{\cdot}C_6H_3Cl{\cdot}O{\cdot}PO(OH)_2,$$

is formed by the action of water on the preceding substance in ethereal solution as a snow-white powder which melts at 161—162°, is hydrolysed to 5-chlorosalicylic acid when boiled with water, and when heated with 1 mol. of phosphorus pentachloride in a sealed tube at 185—190° yields 4-*chloro-2-trichloromethylphenyl dichloro-orthophosphate*, $CCl_3{\cdot}C_6H_3Cl{\cdot}O{\cdot}POCl_2$. This melts at 59—60°, boils at 197° under 15 mm. pressure, and when heated with 1 mol. of phosphorus pentachloride in a sealed tube at 210—220° forms 2 : 5-*dichlorobenzotrichloride*, $C_6H_3Cl_2{\cdot}CCl_3$, which boils at 150° under 13 mm. pressure, and on prolonged boiling with water in a reflux apparatus is hydrolysed, forming 2 : 5-dichlorobenzoic acid. G. Y.

Action of Phosphorus Pentachloride and Trichloride on 3:5-Dibromosalicylic Acid.

RICHARD ANSCHÜTZ and ALFRED ROBITSEK (*Annalen*, 1906, **346**, 323—329. Compare preceding abstracts).—3 : 5-Dibromosalicylic chloride, $OH{\cdot}C_6H_2Br_2{\cdot}COCl$, prepared by heating 3 : 5-dibromosalicylic acid with phosphorus pentachloride in light petroleum solution or in a sealed tube at 100°, forms hard, yellow, crystalline aggregates, melts at 86·5°, and when boiled with water yields 3 : 5-dibromosalicylic acid. The ethyl ester prepared by the action of alcohol on the acid chloride is identical with Freer's ester (Abstr., 1893, i, 66); it crystallises in glistening, rhombic plates [$a : b : c = 0{\cdot}928715 : 1 : 0{\cdot}519089$]. The *anilide*,

$$OH{\cdot}C_6H_2Br_2{\cdot}CO{\cdot}NHPh,$$

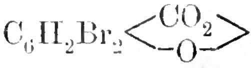
crystallises from alcohol in glistening needles and melts at 139—140°.

4 : 6-*Dibromo-2-trichloromethylphenyl dichloro-orthophosphate*,

$$CCl_3{\cdot}C_6H_2Br_2{\cdot}O{\cdot}POCl_2,$$

formed by heating 3 : 5-dibromosalicylic acid with 2 mols., or the acid chloride with 1 mol. of phosphorus pentachloride in a sealed tube at 100°, crystallises in large, colourless plates and melts at 129—130°.

3 : 5-*Dibromosalicylide*, $(C_7H_2O_2Br_2)_4$, is prepared by slowly heating 3 : 5-dibromosalicylic chloride above its melting point under 12 mm. pressure; it separates from a mixture of chloroform and alcohol as a white, flocculent mass, becomes vitreous at 220°, melts at 230°, and when slowly heated resolidifies at 245—260°, forming a *poly*-3 : 5-*dibromosalicylide*, $(C_7H_2O_2Br_2)_x$, which is obtained as a white powder, melts and decomposes above 285°, is only sparingly soluble in xylene, is insoluble in other organic solvents or aqueous alkali hydroxides, and is not identical with the *isomerisation product* formed slowly from dibromosalicylide at the ordinary temperature.

3 : 5-*Dibromosalicylphosphorous chloride*,  $C_6H_2Br_2{<}\substack{CO_2\\ -O-}{>}PCl$, melts at 75—76°, boils at 210° under 12 mm. pressure, forms an *additive* compound with chlorine, fumes in contact with air, and reacts violently with water, being hydrolysed to 3 : 5-dibromosalicylic acid.

G. Y.

Action of Phosphorus Pentachloride and Trichloride on 3 : 5-Di-iodosalicylic Acid. RICHARD ANSCHÜTZ, ALFRED ROBITSEK, and FRITZ SCHMITZ (*Annalen*, 1906, **346**, 330—335. Compare preceding abstracts).—3 : 5-*Di-iodosalicylic chloride*, $OH\cdot C_6H_2I_2\cdot COCl$, is prepared by heating 3 : 5-di-iodosalicylic acid with 1 mol. of phosphorus pentachloride in benzene solution at 60°; it forms yellow, crystalline, nodular aggregates, melts at 97—98°, does not react with phosphorus oxychloride at 100°, and is hydrolysed rapidly when heated with water.

The *methyl ester*, $OH\cdot C_6H_2I_2\cdot CO_2Me$, formed by the action of methyl alcohol on the acid chloride, melts at 110° and boils and decomposes partially at 221° under 17 mm. pressure. The *ethyl* ester, $C_9H_8O_3I_2$, crystallises in glistening, rhombic leaflets, melts at 133°, and decomposes above 200° when heated under reduced pressure. The *anilide*, $OH\cdot C_6H_2I_2\cdot CO\cdot NHPh$, melts and decomposes at 173·5°.

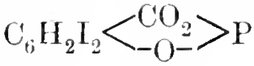
When heated above its melting point under 15 mm. pressure, 3 : 5-di-iodosalicylic chloride forms two di-iodosalicylides. α-3 : 5-Di-iodosalicylide, $(C_7H_2O_2I_2)_x$, separates from a mixture of chloroform and alcohol as a white, flocculent mass, becomes vitreous at 120°, melts at about 145°, is readily soluble in chloroform or xylene, and decomposes liberating iodine when exposed to light.

β-3 : 5-*Di-iodosalicylide*, $(C_7H_2O_2I_2)_x$, formed chiefly at 150°, crystallises from xylene as a white crust, melts at 101°, and is insoluble in chloroform.

4 : 6-*Di-iodo-2-trichloromethylphenyl dichloro-orthophosphate*,

$$CCl_3\cdot C_6H_2I_2\cdot O\cdot POCl_2,$$

prepared by heating 3 : 5-di-iodosalicylic acid with 2 mols. of phosphorus pentachloride in a sealed tube at 100° for ten hours, crystallises from light petroleum in large, stellate aggregates, melts at 126°, and is hydrolysed to 3 : 5-*di-iodosalicylic acid* when boiled with water.

3 : 5-*Di-iodosalicylphosphorous chloride*,  $C_6H_2I_2{<}\substack{CO_2\\ -O-}{>}PCl$, formed by heating 3 : 5-di-iodosalicylic acid with an excess of phosphorus

trichloride, melts at 126°, decomposes when heated under reduced pressure, and is hydrolysed readily by water. G. Y.

Action of Phosphorus Pentachloride and Trichloride on Nitro- and Halogen-nitro-salicylic Acids. Richard Anschütz, Everhard Weber, Julius Sieben, and Richard Anspach (*Annalen*, 1906, **346**, 336—340. Compare preceding abstracts).—3 : 5-Dinitrosalicylic chloride, $OH\cdot C_6H_2(NO_2)_2\cdot COCl$, is prepared by the action of phosphorus pentachloride on 3 : 5-dinitrosalicylic acid in light petroleum solution; it crystallises from a mixture of benzene and light petroleum in small, thin needles, melts at 69—70°, and reacts with methyl and ethyl alcohols, forming the esters which melt at 125° and 98° respectively (Cahours, *Annalen*, 1849, **69**, 230, 235), and are formed also by the action of methyl and ethyl alcohols on the products of the reaction of the acid chloride with methyl and ethyl sodiomalonates. When heated to 70—80°, the acid chloride evolves hydrogen chloride and yields an impure 3 : 5-*dinitrosalicylide*, $(C_7H_2O_6N_2)_x$, which is obtained as a greyish-yellow powder, melts at 150—155°, is hydrolysed by cold water forming 3 : 5-dinitrosalicylic acid, and when treated with ethyl alcohol in chloroform solution forms ethyl 3 : 5-dinitrosalicylate.

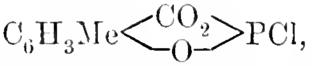
3-*Nitrosalicylic chloride*, $OH\cdot C_6H_3(NO_2)\cdot COCl$, formed in the same manner as the 3 : 5-dinitro-acid chloride, crystallises from a mixture of benzene and light petroleum in sheaves of large, long plates, melts at 59—61°, and is hydrolysed to 3-nitrosalicylic acid when boiled with water.

5-*Chloro*-3-*nitrosalicylic chloride*, $OH\cdot C_6H_2Cl(NO_2)\cdot COCl$, formed from 5-chloro-3-nitrosalicylic acid melting at 163°, could not be purified from phosphorus pentachloride; when treated with alcohol, it yields the ethyl ester, melting at 90—91°.

5-*Bromo*-3-*nitrosalicylic chloride*, $OH\cdot C_6H_2Br(NO_2)\cdot COCl$, separates from a mixture of benzene and light petroleum in stout, yellow crystals and melts at 56·5°.

3-*Bromo*-5-*nitrosalicylic chloride*, $C_7H_3O_4NClBr$, forms stout, white crystals and melts at 95—96°. G. Y.

Action of Phosphorus Pentachloride and Trichloride on β-Cresotic Acid [2-Hydroxy-*m*-toluic Acid; 3-Methylsalicylic Acid]. Richard Anschütz, Ernst Schroeder, Everhard Weber, and Richard Anspach (*Annalen*, 1906, **346**, 341—349. Compare preceding abstracts).—2-*Hydroxy*-m-*toluoyl chloride*, $OH\cdot C_6H_3Me\cdot COCl$, prepared by the action of phosphorus pentachloride on 2-hydroxy-*m*-toluic acid in light petroleum solution, solidifies in a freezing mixture and melts at 27—28°. *Silver* 2-*hydroxy*-m-*toluate*, $OH\cdot C_6H_3Me\cdot CO_2Ag$, forms a white, granular powder, which blackens slowly on exposure to light. The *amide*, $OH\cdot C_6H_3Me\cdot CO\cdot NH_2$, crystallises from dilute alcohol in small, dull, white needles and melts at 112°; the *anilide*, $OH\cdot C_6H_3Me\cdot CO\cdot NHPh$, crystallises in sheaves of needles and melts at 123°; the *piperidide*, $OH\cdot C_6H_3Me\cdot CO\cdot C_5H_{10}N$, forms monoclinic plates [$a : b : c = 1{\cdot}34217 : 1 : 1{\cdot}88072$; $\beta = 77°29{\cdot}5'$] and melts at 53°.

3-*Methylsalicylphosphorous chloride*,  $C_6H_3Me<\begin{smallmatrix}CO_2\\O\end{smallmatrix}>PCl$, prepared by boiling 2-hydroxy-*m*-toluic acid with phosphorus trichloride in xylene solution in a reflux apparatus, melts at 36—37°, boils at 143·6—144° under 14 mm. pressure, and when heated with phosphorus pentachloride forms 3-*chlorocarboxy-o-tolyl dichloro-orthophosphate*, $COCl\cdot C_6H_3Me\cdot O\cdot POCl_2$, which is formed also by the action of chlorine on the fused phosphorous chloride. It is obtained as a transparent liquid, which boils at 185·6—186·2° under 12 mm. pressure and is hydrolysed by moisture.

3-*Methylsalicylphosphoric chloride dibromide*,

$$COBr\cdot C_6H_3Me\cdot O\cdot POClBr$$

or $COCl\cdot C_6H_3Me\cdot O\cdot POBr_2$, prepared by the action of bromine on the phosphorous chloride, is obtained as a transparent oil which boils at 200—202° under 15 mm. pressure, is very unstable, and forms 2-hydroxy-*m*-toluic acid when boiled with aqueous sodium hydroxide.

3-*Trichloromethyl-o-tolyl dichloro-orthophosphate*,

$$CCl_3\cdot C_6H_3Me\cdot O\cdot POCl_2,$$

prepared by boiling 2-hydroxy-*m*-toluic acid with 2 mols. of phosphorus pentachloride in carbon tetrachloride solution in a reflux apparatus, crystallises in prismatic plates, melts at 80°, boils at 199·4—199·8° under 13 mm. pressure, and is hydrolysed readily by water in ethereal solution, forming 3-*carboxytolyl dihydrogen phosphate*,

$$CO_2H\cdot C_6H_3Me\cdot O\cdot PO(OH)_2;$$

this is a white, crystalline substance and melts at 148—149°.

G. Y.

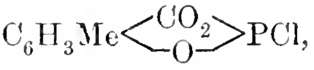
Action of Phosphorus Pentachloride and Trichloride on *m*-Cresotic Acid (3-Hydroxy-*p*-toluic Acid; 4-Methylsalicylic Acid). RICHARD ANSCHÜTZ and ERNST SCHROEDER (*Annalen*, 1906, **346**, 349—353. Compare preceding abstracts).—4-*Chlorocarboxy-3-tolyl dichloro-orthophosphate*, $COCl\cdot C_6H_3Me\cdot O\cdot POCl_2$, formed by the action of phosphorus pentachloride on 3-hydroxy-*p*-toluic acid or by the action of chlorine or phosphorus pentachloride on 4-methylsalicylphosphorous chloride, is obtained as a clear, strongly refracting, viscid liquid, which boils at 184·6—185·4° under 12 mm. pressure, and, when heated with phosphorus pentachloride in a sealed tube at 165—170°, yields 4-*trichloromethyl-3-tolyl dichloro-orthophosphate*,

$$CCl_3\cdot C_6H_3Me\cdot O\cdot POCl_2;$$

this could not be purified from accompanying substitution products.

4-*Chlorocarboxy-3-tolyl metaphosphate*, $COCl\cdot C_6H_3Me\cdot O\cdot PO_2$, prepared by carefully heating the dichloro-orthophosphate with anhydrous oxalic acid and distilling the product under reduced pressure, crystallises in long plates, melts at about 77°, and boils at 195·4—196·2° under 14 mm. pressure.

4-*Carboxy-3-tolyl dihydrogen phosphate*, $CO_2H\cdot C_6H_3Me\cdot O\cdot PO(OH)_2$, formed by the action of water on the dichloro-orthophosphate, melts at 150°.

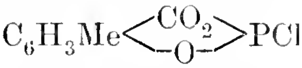
4-*Methylsalicylphosphorous chloride*,  $C_6H_3Me<\begin{smallmatrix}CO_2\\O\end{smallmatrix}>PCl$, prepared by heating 3-hydroxy-*p*-toluic acid with phosphorus trichloride in xylene solution in a reflux apparatus, forms a white, crystalline mass, melts at 45°, and boils at 150—151° under 13 mm. pressure.

4-*Methylsalicylphosphoric chloride dibromide*, $COCl\cdot C_6H_3Me\cdot O\cdot POBr_2$ or $COBr\cdot C_6H_3Me\cdot O\cdot POClBr$, prepared by the action of bromine on 4-methylsalicylphosphorous chloride, is obtained as a clear, viscid liquid, which soon becomes yellow, boils at 202—203° under 13 mm. pressure, and is readily hydrolysed by moisture. G. Y.

Action of Phosphorus Pentachloride and Trichloride on *p*-Cresotic Acid (5-Methylsalicylic Acid; 4-Hydroxy-*m*-toluic Acid). RICHARD ANSCHÜTZ and ERNST SCHROEDER (*Annalen*, 1906, **346**, 354—357. Compare preceding abstracts).—2-*Chlorocarboxy*-p-*tolyl dichloro-orthophosphate*, $COCl\cdot C_6H_3Me\cdot O\cdot POCl_2$, formed by the action of phosphorus pentachloride on 4-hydroxy-*m*-toluic acid or of phosphorus pentachloride or chlorine on 5-methylsalicylphosphorous chloride, is obtained as a transparent, strongly refracting liquid, which boils at 185° under 12 mm. pressure, yields 4-hydroxy-*m*-toluic acid when boiled with water, and when heated with phosphorus pentachloride in a sealed tube at 165—170° forms a *mixture* of products boiling at 183—225° under 13 mm. pressure.

2-*Chlorocarboxy*-p-*tolyl metaphosphate*, $COCl\cdot C_6H_3Me\cdot O\cdot PO_2$, formed by the action of anhydrous oxalic acid or the dichloro-orthophosphate, crystallises from ether in plates, melts at 88°, and boils at 185—186° under 14 mm. pressure.

2-*Carboxy*-p-*tolyl dihydrogen phosphate*, $CO_2H\cdot C_6H_3Me\cdot O\cdot PO(OH)_2$, forms a white, crystalline mass and melts at 139·5—140·4°.

5-*Methylsalicylphosphorous chloride*,  $C_6H_3Me{<}\substack{CO_2\\O}{>}PCl$, melts at 61°, boils at 145·6—146·4° under 12 mm. pressure, and reacts with bromine forming 5-*methylsalicylphosphoric chloride dibromide*,

$$COCl\cdot C_6H_3Me\cdot O\cdot POBr_2$$

or $COBr\cdot C_6H_3Me\cdot O\cdot POClBr$, which solidifies in a freezing mixture and melts in the hand to a transparent oil boiling at 205—207° under 15 mm. pressure; it is easily hydrolysed by water. G. Y.

Action of Phosphorus Pentachloride and Trichloride on 2-Hydroxyuvitic Acid. RICHARD ANSCHÜTZ and ALFRED ROBITSEK (*Annalen*, 1906, **346**, 357—360. Compare preceding abstracts).—2-*Hydroxyuvityl dichloride*, $OH\cdot C_6H_2Me(COCl)_2$ [OH : Me : COCl : COCl = 2 : 3 : 1 : 5], prepared by the action of phosphorus pentachloride on 2-hydroxyuvitic acid in light petroleum solution, crystallises in sheaves of colourless needles, melts at 67—68°, decomposes when distilled under reduced pressure, is moderately stable when exposed to air, and is hydrolysed when heated with water. The dimethyl ester, formed by the action of methyl alcohol on the dichloride, melts at 132° (128°: Jacobsen, Abstr., 1881, 431); the *diethyl* ester, $OH\cdot C_6H_2Me(CO_2Et)_2$, crystallises from light petroleum in colourless needles and melts at 62°. The *dianilide*, $OH\cdot C_6H_2Me(CO\cdot NHPh)_2$, crystallises in transparent prisms which soon become opaque and melts at 238°.

The action of phosphorus trichloride on 2-hydroxyuvitic acid leads to the formation of an extremely hygroscopic, colourless, viscid *oil*, which reacts energetically with water, forming 2-hydroxyuvitic acid. G. Y.

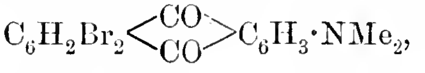
Action of Phosphorus Pentachloride on 1-Hydroxy-2-Naphthoic Acid. Richard Anschütz, Everhard Weber, and Karl Runkel (*Annalen*, 1906, **346**, 360—381. Compare preceding abstracts; Wolffenstein, Abstr., 1887, 963; 1888, 714).—After purification by conversion into the ammonium salt and precipitation by hydrochloric acid, 1-hydroxy-2-naphthoic acid melts at 191—192° (187°: Schmidt and Burkhardt, Abstr., 1888, 59). 1-*Hydroxy-2-naphthoyl chloride*, $OH\cdot C_{10}H_6\cdot COCl$, formed by the action of phosphorus pentachloride on the acid in light petroleum solution, crystallises in long, yellow needles, melts at 85—86°, and when treated with ammonia in ethereal solution yields the *amide* $OH\cdot C_{10}H_6\cdot CO\cdot NH_2$, which forms yellow, granular crystals and melts at 202°. The *anilide*, $OH\cdot C_{10}H_6\cdot CO\cdot NHPh$, forms white, glistening crystals and melts at 154°.

The chief part of this paper consists of a *résumé* and discussion of the results described in this and the preceding papers. G. Y.

3 : 6-Dibromo-2′-dimethylaminobenzoylbenzoic Acid, the Corresponding Diethyl Compound, and their Derivatives. Émile Séverin (*Compt. rend.*, 1906, **142**, 1274—1276. Compare Abstr., 1900, i, 296, 450, 598).—3 : 6-*Dibromo-2′-dimethylaminobenzoylbenzoic acid*, $NMe_2\cdot C_6H_4\cdot CO\cdot C_6H_2Br_2\cdot CO_2H$, prepared by Haller and Guyot's method (compare Abstr., 1894, i, 602) from 1 : 4-dibromophthalic acid (Guareschi, Abstr., 1888, 1300), crystallises from alcohol in magnificent citron-yellow plates and melts at 249°; the *acetate* (mixed anhydride) crystallises from benzene and alcohol in brilliant plates and melts at 195°; the *methyl* ester prepared by the action of sodium methoxide on the acetate forms white, highly refractive crystals which melt at 180°; the *ethyl* ester, similarly prepared, melts at 173°; the *nitroso*-derivative $NO\cdot NMe_2\cdot C_6H_3\cdot CO\cdot C_6H_2Br_2\cdot CO_2H$, prepared by the action of sodium nitrite on the original acid, forms pale yellow needles which melt at 165°.

3 : 6-*Dibromo-2′-dimethylaminobenzylbenzoic acid*,

$$NMe_2\cdot C_6H_4\cdot CH_2\cdot C_6H_2Br_2\cdot CO_2H,$$

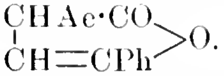
obtained by reducing the corresponding benzoylbenzoic acid, crystallises with difficulty, melts at 253°, and is converted into 1-*dimethylamino-5 : 8-dibromoanthraquinone*,  $C_6H_2Br_2<\substack{CO\\CO}>C_6H_3\cdot NMe_2$, by the prolonged action of concentrated sulphuric acid at 66°; this compound forms bronze-red needles and melts at 218°.

3 : 6-*Dibromo-2′-diethylaminobenzoylbenzoic acid*,

$$NEt_2\cdot C_6H_4\cdot CO\cdot C_6H_2Br_2\cdot CO_2H,$$

forms yellow plates and melts at 221°; the *acetate* forms white plates and melts at 159°, and the *methyl* ester forms refractive crystals and melts at 186°. M. A. W.

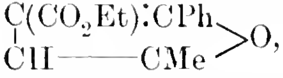
Formation of Unsaturated Ketolactones from αβ-Diacylcarboxylic Esters. Walther Borsche and Albert Fels (*Ber.*, 1906, **39**, 1809—1818).—Ethyl acetophenoneacetoacetate (Paal, Abstr., 1883, 598) is quantitatively obtained from ethyl sodioacetoacetate and ω-bromoacetophenone in ethereal solution. When heated with sodium ethoxide, or when distilled, the ester yields Paal's dehydroacetophenone-acetone-carboxylic acid (Abstr., 1885, 248), which, from its general behaviour and from its resemblance to Knorr's acetylangelicalactone (Abstr., 1899, i, 194; compare also Abstr., 1889, 384; 1897, i, 63), the author concludes to be the lactone of γ-hydroxy-α-acetyl-γ-phenyl-Δ^{β}-butenoic acid,



$\begin{matrix}CHAc\cdot CO\\ CH{=}CPh\end{matrix}\!>\!O.$

It reduces ammoniacal silver solutions, is soluble in alkali carbonates, develops a greenish-blue coloration with ferric chloride, and is reconverted into the parent substance by boiling alcohol. By benzoylation in pyridine, a *benzoate* is obtained, which separates from alcohol in long, rose-red needles, melts at 160—161°, and is converted by phenylhydrazine in alcoholic solution into the *phenylhydrazone* of the original lactone, which crystallises in golden-yellow needles and melts at 168°. The *semicarbazone* melts and decomposes at 264°. C. S.

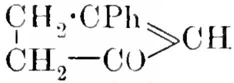
Synthetical Experiments with Ethyl Benzoylacetonylacetate. WALTHER BORSCHE and ALBERT FELS (*Ber.*, 1906, **39**, 1922—1929).—Ethyl benzoylacetonylacetate, $CH_2Ac\cdot CHBz\cdot CO_2Et$, is prepared by heating ethyl sodiobenzoylacetate with iodoacetone in alcoholic solution; it is obtained as a dark-coloured, heavy oil, which decomposes when distilled, forming *ethyl phenuvate*,



$$\begin{matrix}C(CO_2Et){:}CPh\\ CH\text{———}CMe\end{matrix}\!>\!O,$$

which distils at 193—194° under 20 mm. pressure, and on hydrolysis yields phenuvic acid (compare Paal, *Habilitations-schrift*, Wurzburg, 1890). On elimination of carbon dioxide, this acid yields 2-phenyl-5-methylfuran.

1-Phenyl-Δ^1-*cyclo*pentene-3-one,



$\begin{matrix}CH_2\cdot CPh\\ CH_2{-}CO\end{matrix}\!>\!CH$

is formed together with benzoic and lævulic acids when ethyl benzoylacetonylacetate is boiled with 2 per cent. aqueous sodium hydroxide; it is identical with Paal's dehydrophenacylacetone (Abstr., 1884, 1177). The action of 2 per cent. alcoholic potassium hydroxide on ethyl benzoylacetonylacetate at the ordinary temperature leads to the formation of phenacylacetone, which is isolated as the 4-*phenylsemicarbazone*, $C_{25}H_{26}O_2N_6$, crystallising in white needles and melting at 194—195°. When heated with dilute hydrochloric acid, ethyl benzoylacetonylacetate yields ethyl phenuvate, which is hydrolysed and partially decomposed, yielding 2-phenyl-5-methylfuran, together with a small amount of phenyl*cyclo*pentenone.

The action of ammonia on ethyl benzoylacetonylacetate leads to the formation of *ethyl* γ-*amino*-α-*benzoyl*-Δ^{β}-*pentenoate*,

$$NH_2\cdot CMe{:}CH\cdot CHBz\cdot CO_2Et,$$

which readily changes into *ethyl 2-phenyl-5-methylpyrrole-3-carboxylate*, $C_4NH_2MePh\cdot CO_2Et$. The action of aniline on ethyl benzoylacetonylacetate leads to the formation of 1:2-*diphenyl-5-methylpyrrole-3-carboxylate*, $C_4NHMePh_2\cdot CO_2Et$, which crystallises in glistening needles and melts at 133·5°. The *acid*, $C_{18}H_{15}O_2N$, crystallises in glistening, silvery leaflets and melts and decomposes at 267°, forming carbon dioxide and 1 : 2-diphenyl-5-methylpyrrole.

Ethyl benzoylacetonylacetate reacts with semicarbazide in alcoholic solution, forming a *product*, $C_{15}H_{17}O_3N_3$, which crystallises in white needles, melts at 224—226°, and is readily soluble in hot alcohol, together with a small quantity of the sparingly soluble *semicarbazone* of the ketone, $C_{14}H_{16}O_3{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2$, which melts at 255—260°.

The *product*, $C_{20}H_{28}O_2N_4$, of the condensation of ethyl benzoylacetonylacetate with phenylhydrazine crystallises in glistening needles and melts and decomposes at 139—140°. G. Y.

Methyl 4-Aminophthalate and Certain of its Acyl Derivatives.

Marston T. Bogert and Roemer R. Renshaw (*J. Amer. Chem. Soc.*, 1906, **28**, 617—624).—*Methyl 4-aminophthalate*,

$$NH_2{\cdot}C_6H_3(CO_2Me)_2,$$

obtained by the reduction of methyl 4-nitrophthalate, crystallises in alcohol or benzene in white, lustrous plates, and from water in long, hexagonal prisms, melts at 84° (corr.), and is soluble in alcohol, acetone, or chloroform, and slightly so in hot water, carbon tetrachloride, or ether. The *hydrochloride* forms a crystalline mass.

By the action of glacial formic acid on the ester, the *compound*, $C_6H_3(CO_2Me)_2{\cdot}NH{\cdot}CH{:}N{\cdot}C_6H_3(CO_2Me)_2$, is obtained, which forms nearly colourless, microscopic crystals, melts at 179° (corr.), and is soluble in alcohol, hot ethyl acetate, acetone, or benzene. *Methyl 4-acetylaminophthalate*, $NHAc{\cdot}C_6H_3(CO_2Me)_2$, obtained by the action of acetic anhydride on the ester, crystallises in small, colourless plates and melts at 136·5° (corr.). The corresponding *propionyl* derivative crystallises in long, thin, colourless needles and melts at 110·5° (corr.). The iso*butyryl* derivative forms long, thin, colourless needles and melts at 122—123° (corr.). The *benzoyl* derivative forms colourless needles and melts at 132—132·5° (corr.). The m-*nitrobenzoyl* derivative crystallises in nearly colourless scales and melts at 147° (corr.). The p-*nitrobenzoyl* derivative crystallises from alcohol in small, yellow flakes and melts at 202° (corr.).

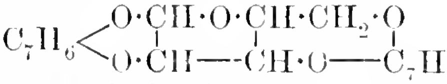
Methyl 4-urethanophthalate, $C_6H_3(CO_2Me)_2{\cdot}NH{\cdot}CO_2Et$, separates from boiling water in long needles and melts at 122° (corr.). *Methyl 4-phenyluraminophthalate*, $C_6H_3(CO_2Me)_2{\cdot}NH{\cdot}CO{\cdot}NHPh$, forms microscopic needles and melts at 138° (corr.).

Methyl 4-ethyloxalylaminophthalate, $C_6H_3(CO_2Me)_2{\cdot}NH{\cdot}CO{\cdot}CO_2Et$, obtained by the action of ethyl oxalate on the ester, crystallises in small, white flakes and melts at 121·5° (corr.). *Methyl oxalyl-4-aminophthalate*, $C_2O_2[NH{\cdot}C_6H_3(CO_2Me)_2]_2$, obtained as a white precipitate in the preparation of the preceding compound, melts at 239° (corr.). The *phthalamic acid*, $C_6H_3(CO_2Me)_2{\cdot}NH{\cdot}CO{\cdot}C_6H_4{\cdot}CO_2H$, forms microscopic crystals and melts at 166—167° (corr.); its *silver* salt is described. The corresponding *succinamic acid* crystallises from water in colourless needles, melts at 173° (corr.), and loses water with probable formation of the imide; the *silver* salt is described. *4-Aminophthalanil*, $NH_2{\cdot}C_6H_3{<}\begin{matrix}CO\\CO\end{matrix}{>}NPh$, obtained by boiling methyl 4-aminophthalate with aniline, crystallises in long, yellow needles and melts at 205·5° (corr.). E. G.

Synthesis of Ethyl Tetrahydroquinonedicarboxylate. HYPOLYT TREPHILIEFF (*Ber.*, 1906, **39**, 1863—1864).—When ethyl sodioacetoacetate (1 mol.) and ethyl γ-bromoacetoacetate react in ethereal solution, a yellow, crystalline substance is obtained, which is Duisberg's ethyl tetrahydroquinonedicarboxylate (Abstr., 1882, 1192).

C. S.

Benzaldehyde Derivatives of Sugars and Glucosides. WILLIAM ALBERDA VAN EKENSTEIN and JAN J. BLANKSMA (*Rec. trav. chim.*, 1906, **25**, 153—161. Compare Lobry de Bruyn and Alberda van Ekenstein, Abstr., 1899, i, 661; 1900, i, 619; 1902, i, 745; and Schiff, Abstr., 1888, 572).—These products are obtained usually by mixing the sugar with benzaldehyde and adding phosphoric oxide gradually with constant stirring. The mixture is set aside for some time and then poured into water, when the condensation product separates usually as a crystalline powder, which is recrystallised from hot methyl alcohol or from chloroform. None of the products reduce Fehling's solution, and all are hydrolysed into their generators by boiling with dilute sulphuric acid.

Dibenzylidenearabinose,  $C_7H_6<\begin{array}{l}O\cdot CH\cdot O\cdot CH\cdot CH_2\cdot O\\ \quad\;\, \vert \qquad\quad\;\; \vert \qquad\qquad\;\; \vert\\ O\cdot CH—CH\cdot O—C_7H_6\end{array}$, melts at 154°, has $[\alpha]_D$ +26·8° in methyl alcohol (showing no mutarotation), and is not acted upon by emulsin at 35°. The number of benzylidene groups present may be determined by boiling a solution of the substance with phenylhydrazine and dilute sulphuric acid and weighing the benzaldehydephenylhydrazone formed.

Dibenzylidenexylose melts at 130°, has $[\alpha]_D$ +37·5°. *Dibenzylidenerhamnose* melts at 128°, has $[\alpha]_D$ +56·3°, and is hydrolysed with difficulty by dilute sulphuric acid.

Amorphous *dibenzylidene* derivatives of dextrose, mannose, galactose, lævulose, and sorbose were obtained, possibly mixed with monobenzylidene derivatives. The crude products react with acetic anhydride, forming *monoacetyl* derivatives. Glucosides condense readily with benzaldehyde when heated with it in presence of anhydrous sodium sulphate. The products do not reduce Fehling's solution, and are hydrolysed by boiling with dilute sulphuric acid.

Benzylidene-α-methylglucoside crystallises from boiling water, melts at 158°, and has $[\alpha]_D$ +85° in aqueous solution. *Benzylidene-β-methylglucoside* melts at 194°, has $[\alpha]_D$ −75° in methyl alcohol, and is not acted on by emulsin. α-Methylmannoside gives rise to both a *mono-* and a *di-benzylidene* derivative. The first melts at 110°, is slightly lævorotatory, and readily soluble in water; the second melts at 178° and has $[\alpha]_D$ −5° in chloroform. *Benzylidene-α-methylgalactoside* melts at 152° and has $[\alpha]_D$ +120·7° in methyl alcohol.

Benzylidenesalicin crystallises from methyl alcohol, melts at 187°, and has $[\alpha]_D$ −48·3° in acetone. *Benzylidenearbutin* melts at 218° and has $[\alpha]_D$ −24·2° in methyl alcohol.

*Di-*p*-toluylidenearabinose*, produced by condensation in presence of phosphoric oxide at the atmospheric temperature, crystallises from methyl alcohol, melts at 164°, and has $[\alpha]_D$ +2·9° in chloroform. The corresponding *xylose* derivative melts at 140°, has $[\alpha]_D$ +45·6° in acetone, and is hydrolysed with difficulty by boiling with dilute sulphuric acid. p-*Toluylidene-α-methylglucoside* melts at 178° and has $[\alpha]_D$ +83·2° in methyl alcohol. The corresponding *derivative* of methylmannoside is a syrup, and has $[\alpha]_D$ +29·5°; that of α-methylgalactoside melts at 146° and has $[\alpha]_D$ +142° in methyl alcohol, and that of salicin melts at 144° and has $[\alpha]_D$ −16° in methyl alcohol.

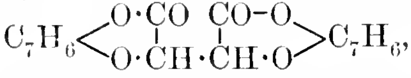
The *product* formed by condensing *β-methylglucoside* with cuminaldehyde in presence of anhydrous sodium sulphate, melts at 124° and has $[\alpha]_D$ −34·8°.

Salicylaldehyde does not condense with sugars in presence of phosphoric oxide, but reacts readily with glucosides. The *α-methylglucoside mono*-derivative separates from warm water in colourless crystals, melts at 182° and has $[\alpha]_D$ +91·2° in water. The *product* formed with salicin melts at 163° and has $[\alpha]_D$ −32° in methyl alcohol.

T. A. H.

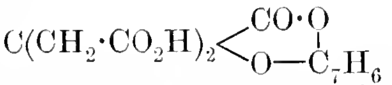
Benzylidene and Toluylidene Derivatives of Hydroxy-acids.

ALBERDA VAN EKENSTEIN and JAN J. BLANKSMA (*Rec. trav. chim.*, 1906, **25**, 162—164. Compare Alberda van Ekenstein, 1901, i, 120; Lobry de Bruyn and Alberda van Ekenstein, 1899, i, 904; 1902, i, 76, and preceding abstract).—*Dibenzylidene*-d-*tartaric acid*,



$$C_7H_6{<}\begin{array}{l}O\cdot CO\quad CO{-}O\\ \quad\ \ |\qquad\ \ |\\ O\cdot CH\cdot CH\cdot O\end{array}{>}C_7H_6,$$

prepared by condensing benzaldehyde with tartaric acid in presence of phosphoric oxide, crystallises from methyl alcohol in long, colourless needles, melts at 145°, has $[\alpha]_D$ +128° in methyl alcohol, and is hydrolysed by boiling dilute sulphuric acid. The similar *condensation product* formed with tolualdehyde crystallises from a mixture of light petroleum and benzene, melts at 177°, and has $[\alpha]_D$ +107° in methyl alcohol. The *l*-tartaric acid *derivative* melts at 166° and has $[\alpha]_D$ −85·8°, and that of racemic acid, which may be obtained from racemic acid or by crystallising together the ditoluylidene derivatives of *d*- and *l*-tartaric acids, melts at 152°.

Benzylidenecitric acid,  $C(CH_2\cdot CO_2H)_2{<}\begin{array}{l}CO\cdot O\\ \quad\ \ |\\ O{-}C_7H_6\end{array}$, prepared by the general method, crystallises from a mixture of benzene and light petroleum and melts at 178°. The *potassium* and *sodium* salts are amorphous; those of barium and calcium are slightly soluble in water. Saccharic, *iso*saccharic, and gulonic acids also condense with benzaldehyde in presence of phosphoric oxide.

T. A. H.

Sulphonation of 2-Chloro-5-nitrobenzaldehyde with Alkali Sulphites.

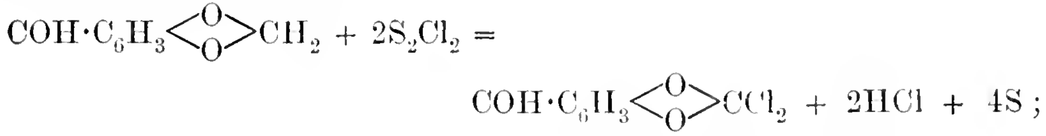
FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 165613).—On boiling 2-chloro-5-nitrobenzaldehyde with aqueous alkali sulphites, sulphonation does occur, but the product is contaminated with a large amount of diazotisable substances. A quantitative yield of 5-nitrobenzaldehyde-2-sulphonic acid is obtained, however, on heating an alcoholic solution of the foregoing aldehyde with sodium sulphite, which remains in suspension in this medium. From the alcoholic filtrate, the sodium salt of the sulphonic acid separates on cooling in yellow crystals.

G. T. M.

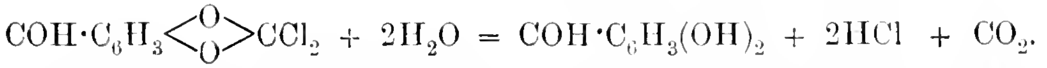
Preparation of Protocatechualdehyde. Franz Fritzsche & Co. (D.R.-P. 162822).—Heliotropin is converted almost quantitatively into protocatechualdehyde by heating at 185—190° under 12 atmospheres pressure with dilute acids or acid metallic salts. The charring which is observed when heliotropin is heated alone at 200° does not take place.

C. H. D.

Preparation of Protocatechuic Aldehyde from Piperonaldehyde or its Chloride. Schimmel & Co. (D.R.-P. 165727).—Piperonaldehyde may be converted directly into protocatechuic aldehyde by heating at 130° with sulphur chloride (S_2Cl_2) until the evolution of hydrogen chloride has ceased, then boiling with water, filtering the solution from precipitated sulphur, and extracting the required aldehyde with ether. The reactions involved may be expressed by the following equations:

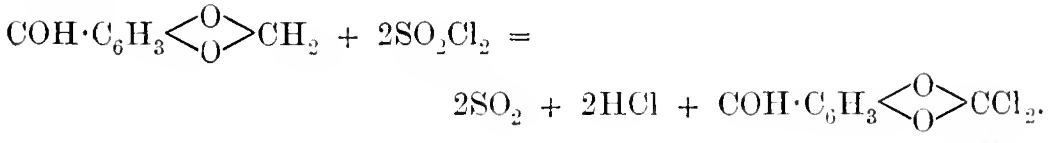


$$COH\cdot C_6H_3{<}\begin{smallmatrix}O\\O\end{smallmatrix}{>}CH_2 + 2S_2Cl_2 = COH\cdot C_6H_3{<}\begin{smallmatrix}O\\O\end{smallmatrix}{>}CCl_2 + 2HCl + 4S;$$



$$COH\cdot C_6H_3{<}\begin{smallmatrix}O\\O\end{smallmatrix}{>}CCl_2 + 2H_2O = COH\cdot C_6H_3(OH)_2 + 2HCl + CO_2.$$

This change may also be effected either with sulphur dichloride (SCl_2) or by passing chlorine into a mixture of sulphur and piperonaldehyde. The chlorination stage of the process may also be effected with sulphuryl chloride, in which case the action takes place as follows:



$$COH\cdot C_6H_3{<}\begin{smallmatrix}O\\O\end{smallmatrix}{>}CH_2 + 2SO_2Cl_2 = 2SO_2 + 2HCl + COH\cdot C_6H_3{<}\begin{smallmatrix}O\\O\end{smallmatrix}{>}CCl_2.$$

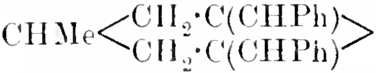
G. T. M.

2-Chloro*cyclo*hexanone and its Derivatives. Louis Bouveault and F. Chereau (*Compt. rend.*, 1906, **142**, 1086—1087).—2-*Chloro*cyclo*hexanone* is obtained by treating *cyclo*hexanone or *cyclo*hexanol in water with chlorine in presence of calcium carbonate. When freshly prepared it is a colourless liquid and boils at 82—83°, but gradually solidifies, forming splendid crystals, and melts at 23°. When boiled with a strong solution of potassium carbonate in water, it passes into 2-*hydroxy*cyclo*hexanone*. This sublimes at 25° under reduced pressure and at 100° under atmospheric pressure, melts at 113° in a closed tube, and is very soluble in warm alcohol, less so in cold, and insoluble in ether or light petroleum. The *semicarbazone* is colourless and melts at 165°. On oxidation with permanganate, it furnishes adipic acid. Nitric acid converts it into oxalic and succinic acids.

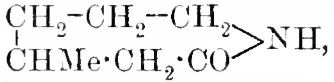
1-*Methyl*-6-cyclo*hexanone*, prepared from 2-chloro*cyclo*hexanone by the Grignard reaction, boils at 160° under 10 mm. pressure; the *semicarbazone* melts at 195°. 1-*Ethyl*-6-cyclo*hexanone* boils at 65° under 10 mm. pressure: its *semicarbazone* melts at 157°. 1-iso*Propyl*-6-cyclo*hexanone* boils at 80° under 10 mm. pressure.

T. A. H.

Terpenes and Ethereal Oils. LXXIX. Compounds of the *cyclo*-Hexanone Series. Otto Wallach (*Annalen*, 1906, **346**, 249—265. Compare Sabatier and Mailhe, Abstr., 1905, i, 275).—The properties of 1 : 2-, 1 : 4-, and 1 : 3-methyl*cyclo*hexanones are compared. Under the conditions described previously (Abstr., 1900, i, 590), the oxime of 1 : 2-methyl*cyclo*hexanone is converted into the iso*oxime*, which crystallises in prisms or needles, melts at 90—91°, and forms an insoluble *hydrochloride*. $C_{17}H_{13}ON,HCl$.

1 : 4-Methyl*cyclo*hexanone, prepared by Sabatier and Mailhe's method (*loc. cit.*), boils at 169—171°; it forms a characteristic, yellow *dibenzylidene* derivative,  $CHMe<\begin{matrix}CH_2{\cdot}C(CHPh)\\CH_2{\cdot}C(CHPh)\end{matrix}>CO$, melting at 98—99°, and an *oxime* melting at 37—39° and boiling at about 114° under 14 mm. pressure. The corresponding iso*oxime*, which is very soluble, yields a solid *hydrochloride*, $C_7H_{13}ON,HCl$.

α-*iso*Oxime of 1 : 3 methyl*cyclo*hexanone (Abstr., 1900, i, 590), melting at 104—105°, must have the constitution

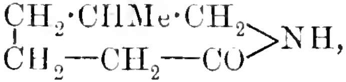


$$\begin{matrix}CH_2{-}CH_2{-}CH_2\\ \vert \\ CHMe{\cdot}CH_2{\cdot}CO\end{matrix}>NH,$$

as when boiled with hydrochloric acid it forms an *amino-acid*,

$$NH_2{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}CH_2{\cdot}CO_2H,$$

which, on oxidation with alkaline permanganate, yields β-methyladipic acid. The β-*iso*oxime of 1 : 3-methyl*cyclo*hexanone,



$$\begin{matrix}CH_2{\cdot}CHMe{\cdot}CH_2\\ \vert \\ CH_2{-}CH_2{-}CO\end{matrix}>NH,$$

when boiled with hydrochloric acid, yields the *hydrochloride* of the amino-acid, $CO_2H{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}CH_2{\cdot}NH_2,HCl$, which, when treated with sodium nitrite and oxidised with chromic acid, forms γ-acetylbutyric acid; the semicarbazone of this melts at 177° (compare Abstr., 1904, i, 752).

The oxime of 3 : 5 : 5-trimethyl*cyclo*hexanone (Abstr., 1902, i, 806) melts at 84—85° (58°: Knoevenagel and Fischer, Abstr., 1897, i, 611); it yields two *iso*oximes: the α-iso*oxime* crystallises in prisms and melts at 111—112°; the more soluble β-iso*oxime* melts at 82—84°.

In addition to the α-*iso*oxime melting at 115—116° (Abstr., 1902, i, 805), a more soluble β-iso*oxime*, melting at 106—108°, has been obtained from the oxime of 2 : 4 : 4-trimethyl*cyclo*hexanone.

[With Karl Hüttner and Johannes Attenburg.]—The base boiling at 273°, obtained by treating 1 : 3-methyl*cyclo*hexanone with ammonium formate (this vol., i, 160; see also Abstr., 1898, i, 485; Tutin and Kipping, Trans., 1904, **85**, 65), consists of two stereoisomeric bases, which are separated by fractional precipitation from the ethereal solution by means of formic acid, the formate of α-dimethyl*cyclo*hexylamine being thrown down before that of the β-stereoisomeride.

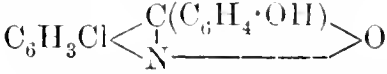
α-*Dimethyl*cyclo*hexylamine* is obtained as an oil, which boils at 273° and forms with water a solid *hydrate*; this melts at 46—48° and liquefies, losing water over sulphuric acid in a desiccator. The *hydrochloride* melts at 285°. The *benzoyl* derivative, $N(C_7H_{13})_2Bz$, crystallises from alcohol in plates, melts at 141°, and has $[\alpha]_D$ − 34 646°; the *nitroso*-derivative, $C_{14}H_{26}ON_2$, crystallises from methyl alcohol, melts at 83—84°, and has $[\alpha]_D$ $-34°$; the *phenylcarbamyl* derivative,

$$N(C_7H_{13})_2\cdot CO\cdot NHPh,$$

melts at 174—176°.

*β-Dimethyl*cyclo*hexylamine* is obtained as an oil which boils at 273° and does not form a hydrate; the *hydrochloride* melts at 211°; the *nitrate* and the *nitrite* are sparingly soluble. The *benzoyl* derivative melts at 151° and has $[\alpha]_D$ $-11·877°$; the *nitroso*-derivative, melting at 62—70°, and the *phenylcarbamyl* derivative, melting at 137—138°, have smaller molecular rotations than the corresponding α-derivatives.

G. Y.

Action of *o*-Nitrobenzaldehyde on Phenols in Presence of Hydrogen Chloride. THEODOR ZINCKE and K. SIEBERT (*Ber.*, 1906, **39**, 1930—1938. Compare Zincke and Preuntzell, this vol., i, 110; Schillinger and Wleügel, Abstr., 1884, 60).—4-Chloro-2-*p*-hydroxyphenylanthroxan,  $C_6H_3Cl\left\langle\begin{matrix}C(C_6H_4\cdot OH)\\ | \\ N\end{matrix}\right\rangle O$, is prepared by saturating a solution of *o*-nitrobenzaldehyde and phenol in glacial acetic acid or methyl or ethyl alcohol, cooled by ice, with hydrogen chloride, or by the action of phosphorus oxychloride on the glacial acetic acid solution; it crystallises in yellow needles, melts at 241°, sublimes without decomposition when heated carefully, is readily soluble in alcohol or acetic acid, but is only sparingly so in ether or benzene, and dissolves in aqueous sodium hydroxide, forming an orange-yellow solution. The dilute alcoholic solution becomes strongly fluorescent on addition of ammonia or an alkali hydroxide. The *acetyl* derivative, $C_{13}H_7O_2ClNAc$, crystallises in broad, colourless needles and melts at 171°.

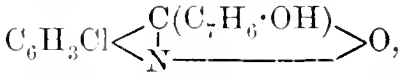
Reduction of the anthroxan by hydriodic acid and phosphorus leads to the formation of 5-*chloro-2-amino-4′-hydroxybenzhydrol*, or by tin and hydrochloric acid in alcoholic or glacial acetic acid solution to the formation of 5-*chloro-2-amino-4′-hydroxybenzophenol*,

$$NH_2\cdot C_6H_3Cl\cdot CO\cdot C_6H_4\cdot OH.$$

This crystallises in glistening, colourless needles, melts at 174°, and dissolves readily in alcohol, in glacial acetic acid forming a red, or in aqueous alkali hydroxides forming a yellow, solution. The *nitrate* and *sulphate* are readily soluble, but the *hydrochloride*, which crystallises in yellow needles, is insoluble in dilute acids. The *diacetyl* derivative, $C_{17}H_{14}O_4NCl$, crystallises in stout, white needles or leaflets and melts at 140°. The action of nitric acid of sp. gr. 1·5 on the amine leads to the formation of an unstable *product*, which is probably a mixture of two nitro-derivatives. When diazotised and coupled with β-naphthol, the amine yields a red *dye*; when boiled, the diazonium sulphate solution evolves nitrogen and yields a *product* which is soluble in aqueous alkali hydroxides; the diazonium chloride is reduced by stannous chloride, forming a yellow precipitate which resinifies when filtered. The *perbromide*, $C_{13}H_6OClBr_3$, prepared from the diazonium chloride, crystallises in red needles and melts at 198°.

5-*Chloro-4′-hydroxybenzophenone*, $C_6H_4Cl\cdot CO\cdot C_6H_4\cdot OH$, formed by the action of amyl nitrite on the amine, crystallises in white needles, melts at 161°, and dissolves readily in alcohol, glacial acetic acid, or aqueous alkali hydroxides. The *acetyl* derivative, $C_{15}H_{11}O_3Cl$, crystallises in white needles and melts at 108°.

5-*Chloro-4′-hydroxybenzhydrol*, $C_6H_4Cl\cdot CH(OH)\cdot C_6H_4\cdot OH$, is prepared by reduction of the ketone by means of sodium amalgam in dilute alkaline solution; it crystallises in white needles and melts at 125°.

4-*Chloro-2-*p*-hydroxy-*m*-tolylanthroxan*, 
$C_6H_3Cl{<}\begin{matrix}C(C_7H_6\cdot OH)\\ | \\ N\end{matrix}{>}O$,
formed from *o*-nitrobenzaldehyde and *p*-cresol, crystallises from alcohol in light yellow needles and melts at 210°; the *alkali* salts crystallise in glistening, orange-yellow leaflets. The *acetyl* derivative, $C_{16}H_{12}O_3NCl$, crystallises in white, glistening leaflets and melts at 135°.

5-*Chloro-2-amino-2′-hydroxy-4′-methylbenzophenone*,

$$NH_2\cdot C_6H_3Cl\cdot CO\cdot C_6H_3Me\cdot OH,$$

formed by reduction of the anthroxan by tin and hydrochloric acid, crystallises in yellow needles, melts at 115°, and dissolves in aqueous alkali hydroxides, forming yellow solutions; the *sodium* salt crystallises in glistening, golden leaflets. The *hydrochloride* forms colourless needles and is hydrolysed by water. The *diacetyl* derivative,

$$C_{18}H_{12}O_4NCl,$$

crystallises in yellow needles and melts at 151°. The action of ethyl nitrite on the amine leads to the formation of a *substance* which separates from alcohol in yellow crystals, and when heated with nitric acid of sp. gr. 1·4 yields 7 *chloro*-1 : 9-*dinitro-2-methylacridone*. This is formed also by treatment of the amino-compound with nitric acid of sp. gr. 1·4; it crystallises in glistening, yellow needles, melts at 250°, and is insoluble in aqueous, but dissolves in aqueous-alcoholic sodium hydroxide, forming a deep red solution, which deposits the *sodium* salt in violet needles, decomposed by water. G. Y.

Action of Benzene and Aluminium Chloride on Free Phenolcarboxylic Chlorides. RICHARD ANSCHÜTZ (*Annalen*, 1906, **346**, 381—391.)—[With JEFF H. SHORES.]—3 : 5-*Dichloro-2-hydroxybenzophenone*, $OH\cdot C_6H_2Cl_2\cdot COPh$, is prepared by heating 3 : 5-dichlorosalicylic chloride with aluminium chloride and benzene in a reflux apparatus and treating the product with dilute hydrochloric acid; it crystallises from alcohol in yellow needles, melts at 116°, is readily soluble in cold benzene or hot alcohol, but dissolves to only a slight extent in water, forming a yellow solution, and with aqueous sodium hydroxide forms a reddish-yellow solution of the *sodium* derivative.

The action of phenylhydrazine on the ketone leads to the formation of (*a*) the *phenylhydrazone*, $OH\cdot C_6H_2Cl_2\cdot CPh{:}N\cdot NHPh$, which crystallises from 96 per cent. alcohol in stellate aggregates of yellow needles, melts at 186°, and is insoluble in water, and (*b*) the *phenylhydrazonium* derivative of the phenylhydrazone,

$$NHPh\cdot N{:}CPh\cdot C_6H_2Cl_2\cdot O\cdot NH_3\cdot NHPh,$$

which crystallises from benzene in long, white, woolly needles. The *oxime*, $OH\cdot C_6H_2Cl_2\cdot CPh{:}N\cdot OH$, crystallises in light yellow, silvery needles and melts at 196°.

3 : 5-*Dichloro-2-hydroxybenzhydrol*, $OH\cdot C_6H_2Cl_2\cdot CHPh\cdot OH$, prepared

by reduction of the ketone with 3 per cent. sodium amalgam in alcoholic solution, crystallises from light petroleum in thin, white needles and melts at 94°.

[With Emanuel Löwenberg.]—3 : 5-*Dibromo-2-hydroxybenzophenone*, $OH{\cdot}C_6H_2Br_2{\cdot}COPh$, formed by the action of aluminium chloride and benzene on 3 : 5-dibromosalicylic chloride, crystallises in long, yellow needles, melts at 129—130°, dissolves in aqueous sodium hydroxide forming a yellowish-green solution, and when treated with phenylhydrazine forms two phenylhydrazones. The stable *phenylhydrazone*, $OH{\cdot}C_6H_2Br_2{\cdot}CPh{:}N{\cdot}NHPh$, crystallises from dilute alcohol in yellow rhomboids and melts at 176—177°. The labile *modification*, which separates from the concentrated mother liquor from the stable form in white crystals, melts and resolidifies, changing into the stable modification at 143°. The labile *oxime*, $OH{\cdot}C_6H_2Br_2{\cdot}CPh{:}N{\cdot}OH$, formed by the action of hydroxylamine on the ketone in alcoholic solution, crystallises in white needles and melts and resolidifies at 175°, changing into the stable *oxime* which melts at 199—201°.

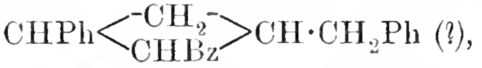
[With Fritz Schmitz.]—3 : 5-*Di-iodobenzophenone*, $OH{\cdot}C_6H_2I_2{\cdot}COPh$, formed from 3 : 5-di-iodosalicylic chloride, crystallises from alcohol in glistening, golden needles and melts at 116°. The *oxime*,

$$OH{\cdot}C_6H_2I_2{\cdot}CPh{:}N{\cdot}OH,$$

crystallises in slightly yellow needles and melts at 127°. G. Y.

Action of a 50 per cent. Mixture of Glacial Acetic and Sulphuric Acids on β-Benzyl-β-styrylpropiophenone and its Derivatives. Hugo Bauer and Ernst Breit (*Ber.*, 1906, 39, 1916—1921. Compare Bauer, Abstr., 1905, i, 278; Kohler, *ibid.*, 358).

—When heated on the water-bath with a mixture of equal parts of glacial acetic and sulphuric acids, β-benzyl-β-styrylpropiophenone undergoes isomerisation, being converted into a *substance*,



$$\mathrm{CHPh}{<}\begin{matrix}\text{-}\mathrm{CH_2}\text{-}\\ \mathrm{CHBz}\end{matrix}{>}\mathrm{CH{\cdot}CH_2Ph}\ (?),$$

which crystallises from alcohol in colourless leaflets, melts at 117°, and remains unchanged when treated with potassium permanganate in acetone solution, but is oxidised slowly to carbon dioxide by aqueous permanganate at 100°. When heated with potassium hydroxide at 300°, it yields benzoic acid and an *acid*, $C_{17}H_{18}O_2$, which crystallises in slender, white needles, melts at 169·5—170°, and is readily soluble in alcohol ; the *barium* salt was analysed. The *oxime*, $C_{24}H_{22}{:}N{\cdot}OH$, crystallises from alcohol and melts at 166° ; the *bromo*-derivative, $C_{24}H_{21}OBr$, crystallises in colourless needles and melts at 161·5°.

Cinnamylidene-p-*methoxyacetophenone*, $C_{18}H_{16}O_2$, prepared by shaking *p*-methoxyacetophenone with cinnamaldehyde in aqueous sodium hydroxide solution, crystallises in light yellow needles, melts at 95·5—96·5°, is readily soluble in alcohol, ether, or acetone, and gives a cherry-red coloration with concentrated sulphuric acid. The *oxime*, $C_{18}H_{17}O_2N$, crystallises in colourless, glistening, silky leaflets, melts at 131·5°, and is readily soluble in alcohol.

β-Benzyl-β-styryl-p-*methoxypropiophenone*,

$$CHPh{:}CH{\cdot}CH(CH_2Ph){\cdot}CH_2{\cdot}CO{\cdot}C_6H_4{\cdot}OMe,$$

is prepared by adding ice-water to a mixture of the cinnamylidene-compound and magnesium benzyl chloride in ethereal solution; it is obtained as a viscid oil, which solidifies under alcohol, forming white needles, melts at 82·5°, and gives a yellowish-green coloration with concentrated sulphuric acid. When heated with glacial acetic and sulphuric acids, it is converted into an *isomeride*, $C_{25}H_{24}O_2$, which forms glistening, white needles, melts at 125°, and is readily soluble in alcohol or acetone.

Cinnamylidene-p-*bromoacetophenone*, $C_{17}H_{13}OBr$, prepared from cinnamaldehyde and *p*-bromoacetophenone, crystallises from acetone in light yellow, matted needles and melts at 149·5°. The *oxime* forms colourless, silky leaflets and melts at 184·5—185·5°.

β-Benzyl-β-styryl-p-*bromopropiophenone*,

$$CHPh{:}CH\cdot CH(CH_2Ph)\cdot CH_2\cdot CO\cdot C_6H_4Br,$$

separates from alcohol in white crystals, melts at 114°, and is readily soluble in alcohol or ether. The *isomeride*, $C_{24}H_{21}OBr$, crystallises in colourless leaflets and melts at 112°. G. Y.

Constitution of α- and β-Benzopinacolins. Maurice Delacre (*Bull. Acad. roy. Belg.*, 1906, 62—70).—A critical *résumé* is given of the known facts regarding the chemistry of the two benzopinacolins (Abstr., 1891, 456; 1896, i, 662; Klinger and Lonnes, Abstr., 1896, i, 691; and Werner and Grob, Abstr., 1904, i, 864), and it is pointed out that the data at present available are insufficient to permit of a formula being definitely assigned to each of these two substances. The author is of opinion that only one benzopinacolin exists and that the variations in structure are not due, as he and others have supposed, to isomerisation induced by the action of reagents, but to an equilibrium phenomenon. T. A. H.

Constitution of Tribenzoylenebenzene. Arthur Michael (*Ber.*, 1906, **39**, 1908—1915).—The constitution originally assigned to tribenzoylenebenzene is the correct one; truxene (tribenzylenebenzene) and allied compounds are derivatives of benzene and not of tetrene.

The preparation of tribenzoylenebenzene from the sodium derivative of ethyl 1 : 3-diketohydrindenecarboxylate is described.

The identity of tribenzoylenebenzene prepared from 1 : 3-diketohydrindene with that prepared from phthalylacetic acid is based essentially on the similarity in physical properties.

The anhydride, $C_{18}H_{10}O_3$, prepared by the action of phosphorus oxychloride on phenylpropiolic acid according to Lanser, is identical with the product which Michael and Bucher obtained by the action of acetic anhydride on phenylpropiolic acid. When this anhydride is dissolved in alkali, it readily forms salts of the dibasic acid, $C_{18}H_{12}O_4$, and when the alkaline solution is acidified, the acid separates and not the anhydride, as Michael and Bucher originally supposed. The acid, $C_{18}H_{12}O_4$, is moderately stable and does not form an appreciable amount of anhydride when heated at 100°; anhydride formation takes place rapidly at 155—165°.

Phenylnaphthalenedicarboxylic acid (Lanser's "diphenyltetrenedicarboxylic acid") is shown to be quite distinct from phenenyltribenzoic acid.

The solubility of the acids in alcohol, glacial acetic acid, and ether respectively is different; the difference between the acids is also indicated by the comparison of their salts quoted. Further, a fluorescein is formed when phenylnaphthalenedicarboxylic acid is fused with resorcinol; phenenyltribenzoic acid does not form a fluorescein. α-Phenylnaphthalene may be isolated from phenylnaphthalenedicarboxylic acid by heating a mixture of the barium salt with barium hydroxide, whilst the hydrocarbon resulting from phenenyltribenzoic acid is triphenylbenzene. A. McK.

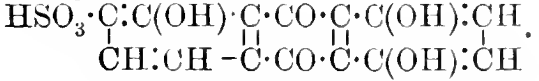
Preparation of Amino-, Alkylamino-, and Arylamino-anthraquinones and their Derivatives. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 165728).—1-*Dimethylamino-5-phenoxyanthraquinone*, $NMe_2\cdot C_6H_3<\substack{CO\\CO}>C_6H_3\cdot O\cdot C_6H_5$, prepared by heating the diphenyl ether of anthrarufin with a 10 per cent. solution of dimethylamine in pyridine at 110—115°, separates from alcohol in red crystals and melts at 147—149°.

1-*Dimethylamino-8-phenoxyanthraquinone*, which separates from alcohol in thick crystals melting at 127—128°, is obtained similarly from the diphenyl ether of chrysazin. This ether also gives rise to 1-*phenylamino-8-phenoxyanthraquinone*, which crystallises from pyridine in long, lustrous needles and melts at 173—174°.

This patent contains several other examples of the substitution of a phenoxy-group by a substituted amino-radicle. In two instances, two amino-groups were introduced into the aromatic nucleus. Thus, 1-phenoxyanthraquinone-5-sulphonic acid when heated with solutions of methylamine and ammonia gave rise to 1 : 5-dimethyldiaminoanthraquinone and 1 : 5-diaminoanthraquinone respectively. G. T. M.

Preparation of Polyhydroxyanthraquinonesulphonic Acids. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 165860).—When the polyhydroxyanthraquinones are sulphonated according to the usual processes, mixtures of sulphonic acids are produced which are difficult to separate, and, moreover, oxidation readily occurs with the introduction of more hydroxyl groups (compare this vol., i, 294). The result is quite different in the presence of boric acid. In this case, homogeneous products are obtained without oxidation.

1 : 4 : 5-Trihydroxyanthraquinone, mixed with an equal weight of boric acid, is treated with twenty parts of fuming 30 per cent. sulphuric acid, at 130°; the product when poured into water gives the free sulphonic acid which is transformed into its acid sodium salt, which separates in orange-red crystals. The new sulphonic acid has probably the following constitution:



$$\begin{array}{l} HSO_3\cdot C{:}C(OH)\cdot C\cdot CO\cdot C\cdot C(OH){:}CH \\ CH{:}CH-C\cdot CO\cdot C\cdot C(OH){:}CH \end{array}.$$

Alizarin-bordeaux when sulphonated in this way also gives rise to a monosulphonic acid. G. T. M.

Presence of *l*-Borneol in the Ethereal Oil from the Buds of Pinus maritima. E. Belloni (*Chem. Centr.*, 1906, i, 1552; from *Boll. Chim. Farm.*, 45, 185—187).—The presence of *l*-borneol in the oil from *Pinus maritima* has been detected by the method X of Tiemann and Krüger (Abstr., 1896, i, 382). In the following table, the physical constants and composition of four samples of oil are given: I and II were prepared from fresh buds, and III and IV partly from dried buds.

	I.	II.	III.	IV.
Yield from buds	0·856	0·867	0·841	0·892
Sp. gr. at 15°	0·8797	0·8805	0·889	0·8848
$[\alpha]_D$ at 15°	−29·4°	−30·48°	−24·45°	−26·17°
n_D at 20°	1·4795	1·4812	1·482	1·478
Free acid calculated as octoic acid...	0·30 %	0·28 %	0·97 %	0·59 %
Esters as bornyl acetate	1·58	1·12	1·67	1·37
Free alcohol (*l*-borneol)	5·08	6·78	5·19	7·83
Combined alcohol	1·25	0·89	1·31	1·07
Total alcohol	6·33	7·67	6·50	8·90

E. W. W.

Chemistry of Bornyl- and Fenchyl-alcohols. Iwan L. Kondakoff (*Chem. Zeit.*, 1906, 30, 497—499). Compare Abstr., 1904, i, 755).—A critical discussion regarding the probable constitution of these substances.

P. H.

Esterification of Alcohols and Phenols. Josef Houben (*Ber.*, 1906, 39, 1736—1753).—The Grignard reagents are employed, in accordance with the equations

$$\mathrm{R{\cdot}OH + R_1MgBr = R{\cdot}OMgBr + R_1H};$$
$$\mathrm{R{\cdot}OMgBr + Ac_2O = R{\cdot}OAc + OAc{\cdot}MgBr};$$

Magnesium alkyl bromides give satisfactory results in the case of saturated primary aliphatic alcohols or phenols, but the unsaturated alcohols, geraniol, linalool, and terpineol, in these circumstances, yield esters which are coloured, contain halogen, and quickly resinify. With such alcohols better results are obtained with magnesium benzyl chloride, but best of all with magnesium alkyl chlorides, when the reaction proceeds almost quantitatively and the ester obtained after fractionation is colourless, free from halogen, and does not exhibit any tendency to become resinous. The operation is performed as follows: the alcohol is slowly added to the cold ethereal solution containing magnesium ethyl or methyl chloride in excess of the theoretical quantity; after keeping at the ordinary temperature for twelve to twenty-four hours, the mixture is well cooled and an excess of acetic anhydride added drop by drop. After one hour, the mixture is decomposed by ice and acetic acid, the ethereal layer removed, dried over potassium carbonate, and the ester fractionated under reduced pressure after evaporation of the ether.

Linalyl propionate is a colourless liquid with an odour of lilies of the valley, and boils at 108—111° under 12 mm. or at 115—119° under 16 mm. pressure.

Terpinyl propionate is a pleasant-smelling liquid which boils at 119—121° under 11·5 mm. pressure. *Cis*-terpin yields a *diacetate*, which boils at 140—141° under 10 mm. pressure and has only a faint odour, differing in these respects from Oppenheim's terpin diacetate (*Annalen*, 1861, **129**, 157), which is probably a mixture of terpinyl acetate, acetic acid, and dipentene, into which the diacetate decomposes when distilled under the ordinary pressure. The terpinyl acetate obtained from this mixture is a different substance from that obtained directly from terpineol. C. S.

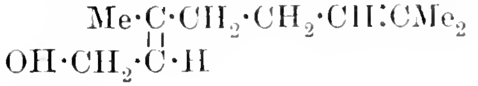
Preparation of the Terpinoid Alcohol, Nerol. HEINE & Co. (D.R.-P. 165894, 165895, 165896. Compare this vol., i, 295).—Nerol is prepared from linalool by the following series of operations: the latter oil was dissolved in glacial acid, treated in the cold with concentrated sulphuric acid dissolved in the same solvent, the oily product washed with water and hydrolysed with alcoholic potash on the water-bath. The hydrolysed oil was distilled in steam and then fractionated under reduced pressure; the less volatile products, consisting of terpineol, geraniol, and nerol, were boiled with phthalic anhydride and benzene, whereby the primary alcohols only were converted into the corresponding acid phthalates. After removing the excess of unchanged anhydride by cooling and adding light petroleum, the solution was distilled and the residual acid phthalates dissolved in dilute aqueous sodium carbonate. The alkaline solution was washed with ether, acidified with dilute sulphuric acid, and the acid phthalates extracted with ether and hydrolysed with alcoholic potash at the ordinary temperature or on the water-bath. The resulting alcohols, geraniol and nerol, were distilled in steam or under diminished pressure and finally separated by means of dry calcium chloride, which yields with geraniol a compound insoluble in light petroleum. The yield of rectified nerol was about 5—10 per cent.

The initial esterification can be accomplished likewise with acetic anhydride, the yield by this method being 15—20 per cent. Other acetylating agents may be employed, such as acetic acid with sodium acetate, ferric chloride, or phosphoric acid. Linalyl acetate and the ethereal oils containing this ester are also amenable to this process of separation. G. T. M.

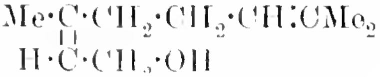
Nerol and its Preparation from Linalool. OTTO ZEITSCHEL (*Ber.*, 1906, **39**, 1780—1792).—When *l*-linalool (Barbier's licarhodol, Abstr., 1893, i, 544) is treated with acetic anhydride, formic acid, or sulphuric and acetic acids (Stephen, Abstr., 1899, i, 68), nerol can be isolated in quantities varying from 3 to 10 per cent.; dilute mineral acids act on linalyl acetate to give a similar poor yield of nerol.

When an alcoholic solution of citral is reduced with sodium amalgam, the resinifying action of the alkali being prevented by the addition of acetic acid drop by drop, geraniol and nerol are produced to the extent of 12 and 7 per cent. respectively. The oxidation of nerol or geraniol by chromic and sulphuric acids yields citral and a substance with the odour of methylheptenone.

Basing his conclusions mainly on these results, the author states that geraniol has the constitution



$$\begin{array}{r} \mathrm{Me{\cdot}C{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CMe_2} \\ \| \qquad\qquad\qquad\quad \\ \mathrm{OH{\cdot}CH_2{\cdot}C{\cdot}H} \qquad\qquad\qquad\quad \end{array};$$

nerol,  $\begin{matrix}\mathrm{Me{\cdot}C{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CMe_2} \\ \| \\ \mathrm{H{\cdot}C{\cdot}CH_2{\cdot}OH}\end{matrix}$; and that citral *a* is identical with geranial and citral *b* with neral.

Terpin hydrate was isolated from the products of the reaction between nerol or geraniol and 5 per cent. sulphuric acid after two hundred hours' shaking (Tiemann, Abstr., 1895, i, 639). The acetates are practically unchanged by this treatment, whilst the linalyl ester is converted more slowly into terpineol and terpin hydrate.] C. S.

Identity of Natural and Artificial Nerols. Hugo von Soden and Walter Treff

(*Ber.*, 1906, **39**, 1792—1793. Compare preceding abstract).—Nerol, obtained from linalool and freed as much as possible from geraniol by calcium chloride, is converted into the diphenylurethane, which is crystallised from light petroleum (Abstr., this vol., i, 295). The recovered nerol agrees in all its properties and in the characteristics of its compounds with the alcohol obtained from natural sources. C. S.

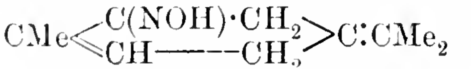
Preparation of the Hydrates of Unsaturated Organic Compounds. Knoll & Co.

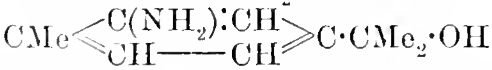
(D.R.-P. 165726).—*Citronellidineacetone hydrate* was obtained by boiling together citronellidineacetone and sodium hydrogen sulphite in aqueous solution, then adding dilute acid, and leaving the mixture for several days, after which the intermediate bisulphite compound was decomposed by sodium hydroxide. The hydrate thus liberated when fractionated under reduced pressure boiled at 175° under 12 mm. pressure.

Carvone hydrate was similarly produced by the successive action of sodium hydrogen sulphite, dilute sulphuric acid, and sodium hydroxide; it boils at 153—154° under 12 mm. pressure and melts at 43°. Its semicarbazone melts at 177° and its oxime at 113°.

Ethyl citrylidenemalonate hydrate, obtained in a similar manner from ethyl citrylidenemalonate, boils at 215—225° under 12 mm. pressure and has a sp. gr. 1·022 at 20°. G. T. M.

Terpenes and Ethereal Oils. LXXX. *iso*Carvoxime and the Constitution of Carvoline. Remarks on the Mechanism of the Isomerisation of Oximes. Otto Wallach

(*Annalen,* 1906, **346**, 266—285. Compare Goldschmidt and Kisser, Abstr., 1887, 475, 923; Goldschmidt, Abstr., 1893, i, 723).—The author discusses the constitution of *iso*carvoxime and of carvoline, and ascribes to these the formulæ  $\mathrm{CMe}\begin{matrix}\mathrm{<C(NOH){\cdot}CH_2>} \\ \mathrm{\lt CH\text{——}CH_2>}\end{matrix}\mathrm{C{:}CMe_2}$ and

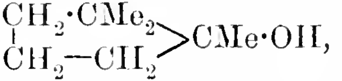
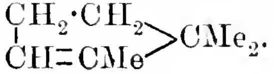


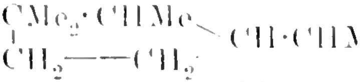
$$\mathrm{CMe}\begin{matrix}\mathrm{C(NH_2){:}CH} \\ \mathrm{CH\text{——}CH}\end{matrix}\mathrm{C{\cdot}CMe_2{\cdot}OH}$$

respectively; the formation of the latter from the former is compared with that of aminothymol from carvoxime. These changes, which resemble that of phenylhydroxylamine into aminophenol, may be explained by the Beckmann reaction, if this is considered to take place through the intermediate formation of a nitrogen heterocyclic group.

[With HERMANN LAUTSCH.]—*iso*Carvoxime was prepared by shaking carvoxime with hydrogen bromide in glacial acetic acid solution and heating the product with sodium methoxide in methyl-alcoholic solution. With bromine it forms a *dibromide*, $C_{10}H_{15}ONBr_2$, melting and decomposing at 126—127°, and a *tetrabromide*, $C_{10}H_{15}ONBr_4$, melting at 134—135°.

Carvoline (Goldschmidt, *loc. cit.*) is formed together with carvacrol when *iso*carvoxime is boiled with dilute sulphuric, acetic, or oxalic acid; it crystallises in colourless needles or prisms, boils at 158—163° under 12 mm. or at 289—290° under the ordinary pressure, and is not volatile in a current of steam; the *hydrochloride* melts at 189—190°. When boiled with fuming hydriodic acid in a reflux apparatus, the base yields carvacrylamine. Carvoline forms dyes when diazotised and coupled with phenols: the *product* with β-naphthol, $OH\cdot C_{10}H_{12}N_2\cdot C_{10}H_7O$, crystallises in deep red needles, melts at 171°, and is insoluble in aqueous alkali hydroxides. The *diazonium sulphate* obtained from carvoline is decomposed by boiling water, forming a *phenol* which yields a deep yellowish-brown dye when coupled with diazotised sulphanilic acid in alkaline solution. The *chloro*-derivative,  $\mathrm{CMe}<\begin{matrix}\mathrm{CCl{:}CH}\\ \mathrm{CH\cdot CH}\end{matrix}>\mathrm{C\cdot CMe_2\cdot OH}$, formed from carvoline by Sandmeyer's reaction, melts at 50—51°, boils at 245—249°, when treated with phosphorus pentachloride yields an oily *dichloride*, boiling at 230—234°, and is oxidised by chromic acid to o-*chloro*-p-*acetyltoluene*, $C_6H_3MeCl\cdot COMe$. This has an odour of acetophenone, melts at 45—46°, boils at 250—254°, and is volatile in a current of steam. The crystalline *semicarbazone* melts at 237—238°; the *oxime*, $C_6H_3Cl\cdot CMe{:}N\cdot OH$, forms white leaflets and melts at 96—97°. When treated with a hypobromite solution, the ketone is oxidised to *o*-chloro-*p*-toluic acid. G. Y.

Synthesis of Camphor Derivatives. *iso*Laurolene and *iso*Lauronolic Acid (β-Campholytic Acid). GUSTAVE BLANC (*Compt. rend.*, 1906, **142**, 1084—1086).—*αα*-Dimethyladipic acid was prepared as already described (Abstr., 1905, i, 680), except that ethyl γ-bromo-*αα*-dimethylbutyrate, $CH_2Br\cdot CH_2\cdot CMe_2\cdot CO_2Et$, was condensed with ethyl malonate in place of ethyl sodiocyanoacetate. The acid was warmed with acetic anhydride and the resulting anhydride converted by distillation into *dimethyl*cyclo*pentanone*,  $\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ |\\ \mathrm{CH_2{-}CO}\end{matrix}>\mathrm{CMe_2}$. This is a mobile liquid, has a camphoraceous odour, and melts at 143°; its *semicarbazone* melts at 190°. The ketone on treatment with magnesium methyl iodide yields the *tertiary alcohol*,  $\begin{matrix}\mathrm{CH_2\cdot CMe_2}\\ |\\ \mathrm{CH_2{-}CH_2}\end{matrix}>\mathrm{CMe\cdot OH}$, which crystallises in long needles, melts at 37°, boils at 60° under 15 mm. pressure, and possesses a musty, camphoraceous odour. When distilled under atmospheric pressure, it decomposes into water and *iso*laurolene,  $\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ |\\ \mathrm{CH{=}CMe}\end{matrix}>\mathrm{CMe_2}$. The hydrocarbon is transformed by condensation with acetyl chloride in presence of aluminium chloride into a *ketone*, which is reduced by sodium to the secondary *alcohol*,



$$\begin{array}{l} CMe_2\cdot CHMe \diagdown \\ | \qquad\qquad\qquad\quad CH\cdot CHMe\cdot OH \\ CH_2 — CH_2 \diagup \end{array}$$

which boils at 90—95° under 10 mm. pressure, and this on oxidation by nitric acid gives dihydro*iso*lauronolic acid, which on bromination in the α-position and subsequent elimination of hydrogen bromide gives *iso*lauronolic acid.

T. A. H.

Ethereal Oils. Heinrich Haensel (*Chem. Centr.*, 1906, i, 1497; from *Geschäftsber.*, March, 1906. Compare Abstr., 1903, i, 187).—Silver fir oil from Lower Austria has almost the same sp. gr. as the Tyrolese oil, but it has a less rotatory power and contains a smaller quantity of esters; it has sp. gr. 0·8761—0·8776 at 15°, $[\alpha]_D$ $-35·99°$ to $-37·14°$ at 15°, and contains 4·46—5·22 per cent. of esters calculated as bornyl acetate. The fruit from which the seeds have been removed yields 0·038 per cent. of an orange-coloured oil which has a strong odour of the fruit and an acid reaction: it has a sp. gr. 0·90735 at 20°, $[\alpha]_D$ $+0·40°$ at 19° (10 per cent. benzene solution), and acid number 22·1. The oil contains aldehydes, and a stearoptene is precipitated on the addition of absolute alcohol.

Dried garden rue yields 0·135 per cent. of a dark brown, ethereal oil which has a very strongly acid reaction and on rectification forms a pale greenish-yellow oil, which has a sp. gr. 0·8487 at 20°, $[\alpha]_D$ $+0·64°$ at 20°, and ester number 119; the acetyl derivative has ester number 157. When shaken with a solution of sodium hydrogen sulphite, the oil does not yield an additive compound.

E. W. W.

Ethereal Oils. Schimmel & Co. (*Chem. Centr.*, 1906, i, 1497—1498; from *Geschäftsber.*, April, 1906. Compare Abstr., 1905, i, 536).—Lemon-yellow cedar oil from Haiti has an odour similar to that of ordinary cedar oil, sp. gr. 0·9612 at 15°, $[\alpha]_D$ $-14°58'$, acid number 2·7, and ester number 5·0; the acetyl derivative has ester number 64. Fennel oil contains camphene and phellandrene, but not cymene (compare Tardy, Abstr., 1897, i, 578). Templin oil prepared from Styrian material has a sp. gr. 0·8685 at 15°, $[\alpha]_D$ $-11°3'$, acid number 1·4, and ester number 16·8 (= 5·9 per cent. bornyl acetate); 67 per cent. of the oil distils at 170—203°. Styrian silver fir oil has sp. gr. 0·8852 at 15°, $[\alpha]_D$ $-34°55'$, and ester number 17·5 (= 6·1 per cent. bornyl acetate); 55 per cent. of the oil distils at 162—185°. Two black pine oils prepared from needles of *Pinus Laricio* have sp. gr. 0·8646 and 0·8701 at 15°, $[\alpha]_D$ $+8°17'$ and $+3°29'$, and ester numbers 2·9 and 9·8 respectively. Bay-leaf oil contains linalool and the methyl ether of eugenol. Bright yellow sassafras oil prepared from the roots of *Sassafras officinalis* dissolves in 1—2 volumes of 90 per cent. alcohol, and has a sp. gr. 1·075 at 15°, $[\alpha]_D$ $+2°14'$, and ester number 1·9. Solidago oil, or oil of Golden Rod, is pale yellow, and has a pleasant, refreshing odour; it has a sp. gr. 0·8904 at 15°, $[\alpha]_D$ $+15°34'$, and ester number 34·2 (acetyl derivative 59·9). The esters probably consist mainly of bornyl acetate. The bright olive-green oil from *Solidago nemoralis* has a peculiar odour, resembling that of cypress oil; it has a sp. gr. 0·8799 at 15°, $[\alpha]_D$ −23°10′, and ester number 14·4 (acetyl derivative 38·2). Indian turpentine oil from the resinous balsam of *Pinus longifolia* is soluble in 7·5 volumes of 90 per cent. alcohol, and has a sp. gr. 0·8734 at 15°, $[\alpha]_D$ +3°13′, acid number 1·9, and ester number 1·3.

An ethereal oil which contains free fatty acids and constituents which cannot be saponified is obtained by extracting musk with ether and distilling in steam. The odour of musk is caused by the presence of a ketone, *muskone*, $C_{15}H_{28}O$ or $C_{16}H_{30}O$, which boils at 327—330° and at 142—143° under 752 and 2 mm. pressure respectively; it has sp. gr. 0·9268 at 15°, $[\alpha]_D$ −10°6′, and n_D 1·47900 at 25°. The *semicarbazone* melts at 133—134°. E. W. W.

Ethereal Oil of the Buds of Pinus maritima. E. Belloni (*Chem. Centr.*, 1906, i, 360—361; from *Ann. Soc. Chim. Milano*, ii).—The fresh buds of *Pinus maritima* collected in S. France yield on distillation 0·517 per cent. of a bright green ethereal oil, which has a fresh, aromatic taste and the characteristic odour of pine needles; the dry buds yield 0·681 per cent. of a similar oil. The following data refer respectively to the oil from the fresh buds and to that from the dry buds. Sp. gr. at 15°, 0·8810 and 0·8963; $[\alpha]_D$ at 15°, −26·518° and −22·355°; acid numbers, 0 and 5·43; ester numbers, 7·90 and 8·27; saponification numbers, 7·90 and 13·70; esters, 2·77 and 2·92 per cent.; combined alcohols, 2·13 and 2·28 per cent. The oil from the dried buds also contained 11·90 of uncombined alcohols and a total of 14·18 per cent. of alcohols. The oil is miscible with 95—100 per cent. alcohol, is soluble in 10 parts of 90 per cent. alcohol, but insoluble in 80 per cent. alcohol, and does not contain aldehydes. The free acids consist mainly of hexoic acid, of which the oil contains 1·396 per cent., and the esters appear to be acetates, propionates, hexoates, and laurates. *l*-Pinene is the chief constituent of the oil. When the alcoholic solution of *l*-pinene nitrosochloride is heated with piperidine for a long time on the water-bath, needle-shaped crystals of nitrosopinene separate from the product after some days. Neither phellandrene nor silvestrene could be detected in the fraction of the oil boiling at 170—190°, but limonene appeared to be present either in the form of one of the two active modifications or in the inactive form as dipentene. Although the odour of the oil indicates the presence of ethers of borneol, attempts to isolate these compounds from the fractions boiling at 190—260° failed. E. W. W.

The Constituents of the Gutta-percha from Palaquium treubi. Émile Jungfleisch and Henri Leroux (*Compt. rend.*, 1906, **142**, 1218—1221).—The crude gutta of the leaves of *Palaquium treubi* contains a crystalline principle, *paltreubin*, $C_{30}H_{50}O$, which remains dissolved when the hot toluene extract of the leaves is treated with alcohol in order to precipitate the hydrocarbon of the gutta, and is separated by evaporating the mother liquor to dryness, extracting the wax from the residue by means of hot alcohol, and finally recrystallising from benzene. *Paltreubin* forms colourless, silky needles belonging to the monoclinic system (Wyrouboff), it melts at 260°, and sublimes at 230°, forming characteristic elongated prisms; it is almost insoluble in all the ordinary organic solvents except toluene or benzene, and its solutions are optically inactive. Paltreubin is completely esterified when heated with excess of acetic anhydride in sealed tubes at 175°; the product consists of two isomeric acetates from which two alcohols, each isomeric with the original, are obtained by saponification.

α-Paltreubyl acetate, $C_{30}H_{49}\cdot OAc$, melts at 235°, is soluble in ether, and can be recrystallised from benzene in the form of voluminous crystals or monoclinic prisms (Wyrouboff); its solutions are optically inactive, and it yields *α-paltreubyl alcohol*, $C_{30}H_{49}\cdot OH$, on saponification with alcoholic potassium hydroxide, which crystallises from benzene in needles melting at 190°. *β-Paltreubyl acetate*, $C_{30}H_{49}\cdot OAc$, melts at 290°, is sparingly soluble in ether, crystallises from benzene in well-developed, colourless prisms belonging to the monoclinic system, but different from those of the α-isomeride (Wyrouboff); *β-paltreubyl alcohol*, $C_{30}H_{49}\cdot OH$, obtained from the preceding compound by saponification with alcoholic potassium hydroxide, crystallises from benzene in long, thin needles, melts at 295°, and sublimes at 270—275°, forming thin, prismatic needles, and is identical with an alcohol which the authors have extracted from the leaves of *P. gutta* or *P. borneese*, or from a residue obtained in the commercial preparation of gutta from leaves.

Paltreubin and α- and β-paltreubyl alcohol are isomeric with α- and β-amyrin (Vesterberg, Abstr., 1887, 733; 1891, 165). M. A. W.

Sapotoxin and Sapogenin from Agrostemma githago. Josef Brandl [with E. Mayr and A. Vierling] (*Chem. Centr.*, 1906, i, 1350—1353; from *Arch. exp. Path. Pharm.*, **54**, 245—284).—The seeds of *Agrostemma githago* contain 6·44 per cent. of fat and yield 4·9—6·1 of crude sapotoxin. 18·1 per cent. of pure sapotoxin is obtained from the crude product by extraction with absolute alcohol, the insoluble residue consisting of a higher sapotoxin. The pure sapotoxin is dull brownish-yellow and contains C 54·23 per cent., H 7·23, and O 38·54; it forms a bright yellow solution in water, and the rotatory power of a 2 per cent. solution in a 20 cm. tube is +0·22°. A determination of the molecular weight by Raoult's method gave 1810. Sapogenin, prepared by digesting sapotoxin with dilute sulphuric acid, contains 66·28 per cent. of carbon, 8·62 of hydrogen, and 25·10 of oxygen, crystallises from absolute alcohol in very small, slender needles, becomes yellow at 190°, sinters at 210°, and decomposes at 220°; it is a saturated acid and liberates carbon dioxide from carbonates. The rotatory power of a 2 per cent. solution in sodium carbonate solution in a 20 cm. tube is +1·6°. Molecular weight determinations by Raoult's method gave 605 and 648, and by the boiling point method 643 and 662. 51·92 per cent. of a sugar (calculated as dextrose) is also formed by the hydrolysis of sapotoxin; it is inactive, is scarcely attacked by yeast in twenty-four hours, and forms three osazones melting respectively at 180°, 203°, and 205°. By the action of acetic anhydride on sapogenin, an acetyl derivative which crystallises from methyl alcohol is formed, together with a by-product which is soluble in water, gives a precipitate with lead acetate, but has no hæmolytic action. The potassium and sodium salts of sapogenin crystallise in slender needles, and the potassium salt of methylsapogenin in very slender rods.

Sapogenin, $C_{33}H_{52}O_{10}$, prepared by the action of dilute sulphuric acid on quillajic acid or on quillajasapotoxin, crystallises from absolute alcohol in slender, white needles; a determination of the molecular weight by the boiling-point method gave 561.

The physiological action of *Agrostemma* sapotoxin and sapogenin is also described in some detail in the abstract. E. W. W.

Products extracted from Solanum sodomaeum. II. Giuseppe Oddo and Amedeo Colombano (*Gazzetta*, 1906, **36**, i, 310—313. Compare Abstr., 1905, i, 455).—The authors describe a method for extracting solanine from *Solanum sodomaeum* more simply and in better yield than by the process formerly described (*loc. cit.*). The berries are well pounded in a marble mortar and are then macerated for twenty-four hours with sufficient 2·5 per cent. sulphuric acid solution to cover them completely. The solution is then filtered through flannel, the filtrate rendered alkaline with sodium or potassium hydroxide solution and the precipitated solanin filtered through flannel, washed well with water, dried, and treated with alcohol as previously described.

The neutralised acid extract is found to contain also a compound which crystallises from water in aggregates of small, reddish-yellow prisms, beginning to melt at 195° and completely melting and decomposing at 215°. Its aqueous solution is coloured green by ferric chloride solution and an intense blood-red by alkali. Alkali carbonate solutions dissolve it, giving brownish-yellow liquids. T. H. P.

Solanine and other Constituents of the Berries of Solanum sodomaeum from Sicily. Arturo Soldaini (*Chem. Centr.*, 1906, i, 563; from *Boll. Chim. Farm.*, 1905, **44**, 769—773, 808—810, and 843—885).—The author concludes that neither he nor Oddo and Colombano (Abstr., 1905, i, 455) have yet been dealing with the pure alkaloid (glucoside), and therefore many of his previously published results require modification. P. H.

Aloxanthin. Otto A. Oesterle (*Chem. Centr.*, 1906, i, 367—368; from *Schweiz. Woch. Pharm.*, **43**, 682—684. Compare Abstr., 1899, i, 538).—Alochrysin is not a homogeneous compound, since the acetyl derivative can be separated into two components, of which the one is insoluble in benzene and a derivative of rhein, whilst the other is a derivative of aloemodin. It is probable that emodin is first formed by the action of potassium dichromate and sulphuric acid on aloin and is then oxidised to rhein. It should doubtless be possible to obtain emodin in this way. E. W. W.

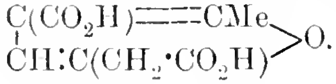
Condensation Products of Tannic Acid with Formaldehyde and Acid Amides. Arnold Voswinkel (D.R.-P. 165980).—The condensation products of tannic acid with formaldehyde and acid amides have the general formula $C_{14}H_9O_9{\cdot}CH_2{\cdot}NH{\cdot}COR$.

The formamide derivative, $C_{16}H_{13}O_{10}N$, which was prepared by adding formaldehyde and formamide to a solution of tannic acid in dilute hydrochloric acid, forms a light brown powder insoluble in water or alcohol.

Methylene-tannin-acetamide, $C_{17}H_{15}O_{10}N$, was obtained similarly and resembles the preceding compound. The derivatives of amides sparingly soluble or insoluble in water were prepared in alcoholic solutions. These products are all soluble in aqueous solutions of sodium carbonate, borate, or acetate, and are regenerated on treatment with acids. The compounds have therapeutic properties similar to those of the carbamide derivatives. G. T. M.

Constitution of Methronic Acid. HYPOLYT TREPHILIEFF (*Ber.*, 1906, **39**, 1859—1862. Compare Fittig and Hantzsch, Abstr., 1889, 126).—Ethyl methronate does not react with phenylhydrazine; the acid is oxidised by nitric acid to acetic and oxalic acids, combines with four atoms of bromine, and is hydrolysed to acetonylacetone. Under Fittig's conditions of preparation, 40 per cent. of the sodium succinate remains in the mother liquor without any ethyl acetoacetate, and the yield is only 30 per cent. of the theoretical; this is increased to 58 per cent. when 2 mols. each of ethyl acetoacetate and acetic anhydride are used for each mol. of sodium succinate. The by-products in the reaction are carbon dioxide, ethyl acetate, and acetone.

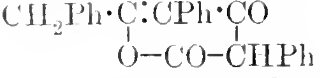
In accordance with these facts, methronic acid is regarded as having the formula



$$\left.\begin{array}{l}\mathrm{C(CO_2H){=\!=\!=}CMe}\\ \mathrm{CH{:}C(CH_2{\cdot}CO_2H)}\end{array}\right>\mathrm{O}.$$

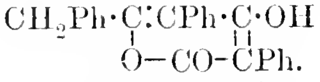
C. S.

Synthesis of Simple Pyronones from Acid Haloids. EDGAR WEDEKIND (*Chem. Centr.*, 1906, i, 369; from *Verh. Deut. Naturforsch. Aerzte*, 1904, ii, 81—83. Compare Abstr., 1901, i, 639; 1902, i, 739).—When propionyl, phenylacetyl, or hydrocinnamoyl chloride acts on tertiary bases, the acid chloride residues unite to form trimeric condensation products. Hydrocinnamoyl chloride yields benzyldiphenyl pyronone, which reacts in accordance with the tautomeric formulæ



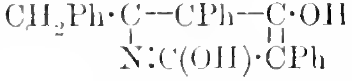
$$\begin{array}{l}\mathrm{CH_2Ph{\cdot}C{:}CPh{\cdot}CO}\\ \qquad\mathrm{O{-}CO{-}CHPh}\end{array}$$

or



$$\begin{array}{l}\mathrm{CH_2Ph{\cdot}C{:}CPh{\cdot}C{\cdot}OH}\\ \qquad\mathrm{O{-}CO{-}CPh.}\end{array}$$

The pyronone forms a sodium salt when treated with sodium hydroxide, and an oxime with hydroxylamine. By the action of acyl chlorides, acyl derivatives are obtained, and benzyldiphenyl dihydroxypyridine,



$$\begin{array}{l}\mathrm{CH_2Ph{\cdot}C{-}CPh{-}C{\cdot}OH}\\ \qquad\quad\mathrm{N{:}C(OH){\cdot}CPh}\end{array}$$

, is formed by the action of ammonia.

When *iso*butyl chloride acts on tertiary bases, a diketone of the tetramethylene series seems to be produced. E. W. W.

Thioindigo-red B. R. WIRTHER (*Chem. Centr.*, 1906, i, 1353; from *Färberzeit.*, **17**, 85—87).—Thioindigo-red,

$$\mathrm{C_6H_4}\!<\!\begin{array}{c}\mathrm{CO}\\ \mathrm{-S-}\end{array}\!>\!\mathrm{C{:}C}\!<\!\begin{array}{c}\mathrm{CO}\\ \mathrm{-S-}\end{array}\!>\!\mathrm{C_6H_4},$$

manufactured by Kalle & Co., of Biebrich, resembles indigo in its method of application as a dye, its solubility in concentrated sulphuric acid, and its slight solubility in organic solvents. It can be sublimed, and its solutions in chloroform, carbon disulphide, toluene, &c., have a yellowish-red fluorescence. Wool, silk, and cotton extract the colouring matter from the yellow solution formed by the action of reducing agents on the dye, and the red dye is regenerated when the fibres are exposed to air. Thioindigo-red may be used with a sodium sulphide bath, and may also be applied in cotton printing. E. W. W.

Constitution of Adrenaline. ERNST FRIEDMANN (*Beitr. chem. Physiol. Path.*, 1906, **8**, 95—120. Compare Abstr., 1901, i, 1069; also Takamine, Abstr., 1902, ii, 217; Aldrich, 1901, ii, 564; 1902, ii, 518; Abel, *ibid.*, 1903, i, 376; von Fürth, *ibid.*, 669; Pauly, 1904, i, 128, 540; Jowett, Trans., 1904, **85**, 192; Bertrand, Stolz, 1905, i, 106).—A modified method for the preparation of von Fürth's adrenaline tribenzenesulphonate is described. In chloroform solution it has $[\alpha]_D$ −15·12°, but the rotation is somewhat less after it has been warmed with acetic acid. The presence of a free hydroxyl group has been shown by its conversion into the m *nitrobenzoate*, $C_{34}H_{28}O_{12}N_2S_3$, which is doubly refracting. It begins to sinter at 71° and melts between 80° and 86°.

When adrenaline tribenzenesulphonate is oxidised with an acetic acid solution of chromic anhydride, it yields *adrenalone tribenzenesulphonate*, $(SO_2Ph\cdot O)_2C_6H_3\cdot CO\cdot CH_2\cdot NMe\cdot SO_2Ph$, which may be purified by solution in acetic acid and precipitation with water. It dissolves sparingly in cold benzene or ethyl acetate and in hot alcohol, and is insoluble in ether, acids, or alkalis. It is optically inactive, and may be crystallised from acetic acid at 0°, and then separates from absolute alcohol in long, rhombic needles melting at 106—107°. Its p-*nitrophenylhydrazone*, $C_{33}H_{28}O_{10}N_4S_3$, melts at 174—175°.

The substance previously termed peradrenalone tribenzenesulphonate is shown to be a mixture of adrenalone and a more complex substance melting at 196—197°. It dissolves in ammonium hydroxide solution.

Adrenalone tribenzenesulphonate has been synthesised from methylaminoacetylcatechol. J. J. S.

Quinine Tannate. MAXIMILIAN NIERENSTEIN (*Chem. Centr.*, 1906, i, 1417; from *Collegium*, 1906, 108).—*Quinine tannate* forms a white, amorphous powder which melts at 64°; it separates from a solution in alcohol to which 4—5 drops of acetic anhydride are added in crystals which melt at 79—81°. Since neither tannin nor gallic acid is formed when the tannate is hydrolysed, it cannot be a true salt, but is possibly a compound resembling a Schiff's base. E. W. W.

Action of Gum Arabic on Morphine. RICHARD FIRBAS (*Chem. Centr.*, 1906, i, 374; from *Pharm. Post.*, **38**, 735—738. Compare Bourquelot, *J. Pharm. Chim.*, [vi], **19**, 475).—An oxymorphine is formed by the action of a solution of gum arabic on morphine, although comparatively slowly, the action being dependent on the concentration of the solution and the time. If the quantity is not too small, the presence of oxymorphine may be detected by the precipitate which it gives with potassium chromate. The gum does not appear, however, to have any action on opium powder or extract even when the substances are allowed to remain together in a moist condition for six weeks. E. W. W.

Morphine Alkylbromides. J. D. Riedel (D.R.-P. 165898).—*Morphine methobromide*, prepared by shaking together for eight to twelve hours at 40—50° a mixture of finely-divided morphine, methyl bromide, and absolute alcohol, was recrystallised from water or dilute alcohol and separated in colourless needles, sintering at 260° and melting at 265—266°. It is only sparingly soluble in absolute alcohol or chloroform, and is insoluble in ether. The same salt was also obtained when finely-divided morphine was suspended in a mixture of chloroform and methyl sulphate, and shaken at the ordinary temperature for one day, when the methosulphate separated. This salt was dissolved in water and treated with concentrated aqueous potassium bromide or any other soluble bromide, when the required methobromide was precipitated.

Morphine ethobromide was obtained from the corresponding ethiodide by treating the latter with moist silver bromide; it crystallises from water or alcohol in colourless needles melting at 245°. These quaternary salts have the narcotic action of morphine, but are far less poisonous. G. T. M.

The Alkyl Bromides of the Alkyl Ethers of Morphine. J. D. Riedel (D.R.-P. 166362).—*Codeine methobromide*, $C_{19}H_{24}O_3NBr$, which is a white, crystalline powder melting at 261°, can be obtained by any of the following processes: from codeine and methyl bromide in dry chloroform, alcoholic, or acetone solution; by double decomposition from the methosulphate and lead bromide; by the methylation of morphine methobromide with sodium ethoxide and methyl bromide.

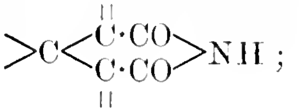
Codeine ethobromide, $C_{20}H_{26}O_3NBr$, produced from the corresponding ethiodide by the action of moist silver bromide, crystallises from acetone in lustrous needles, which contain acetone of crystallisation; these sinter at 70° and melt at 74°. When dried at 100—120°, the substance loses acetone, and then melts at 244—245°.

Codethyline methobromide, $C_{20}H_{26}O_3NBr,H_2O$, is obtained either by evaporating a solution of codethyline methylammonium hydroxide with hydrobromic acid or by treating the methochloride (obtained either from the iodide with moist silver chloride or from the methosulphate with potassium chloride) with saturated aqueous potassium bromide; it crystallises in needles, which, after drying at 120°, melt at 267—268°.

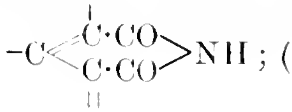
Codethyline ethobromide, $C_{21}H_{28}O_3NBr$, produced by ethylating morphine at 80° with ethyl bromide and alcoholic potash, crystallises in soft, lustrous needles containing 3 or $4H_2O$; after dehydrating, it melts at 225°. G. T. M.

Products of Hydrogenation of Pyrrole by means of Reduced Nickel. Maurizio Padoa (*Atti R. Accad. Lincei*, 1906, [v], **15**, i, 219—223).—By passing a mixture of pyrrole vapour and hydrogen through a tube containing reduced nickel (from the reduction of nickel carbonate in hydrogen at 350°) at 180—190°, the author obtains: (1) a 25 per cent. yield of pyrrolidine, and (2) a small quantity of a hexahydroindoline (?), which gives a *picrate*, $C_8H_{15}N,C_6H_3O_7N_3$, crystallising from alcohol in yellow needles melting at 123°. T. H. P.

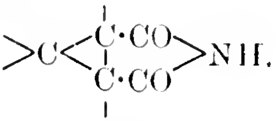
Invertive Power of Certain Pseudo-acids having Complex Functions. RODOLFO TORRESE (*Atti R. Accad. Sci. Torino*, 1906, 41, 309—327).—The author has examined, with regard to their capability of hydrolysing sucrose, a number of derivatives of glutaconimide having formulæ represented by the following schemes:

(1) 

$>C<\begin{matrix}\overset{\parallel}{C}\cdot CO \\ \underset{\parallel}{C}\cdot CO\end{matrix}>NH$;

(2) 

$-C\begin{matrix}\overset{|}{\lessdot}C\cdot CO \\ \lessdot\underset{\parallel}{C}\cdot CO\end{matrix}>NH$;

(3) 

$>C<\begin{matrix}\overset{|}{C}\cdot CO \\ \underset{|}{C}\cdot CO\end{matrix}>NH$.

Compounds of types (1) and (3) are unable to hydrolyse sucrose, whilst those of type (2) are able to do so. In order, therefore, that they may exhibit this property, the molecules must possess a double linking in the position shown in (2), and they must, further, have the two carbonyl groups unsubstituted; if, for instance, one of the carbonyl groups is replaced by CMe_2, the power to invert sucrose is lost.

T. H. P.

A New Class of Salt-forming Metallic Hydroxides. PAUL PFEIFFER [with M. TAPUACH and W. OSANN] (*Ber.*, 1906, 39, 1864—1879. Compare Abstr., 1902, i, 728).—*Dihydroxylodiaquodipyridinechromium bromide*, $[CrPy_2(OH_2)_2(OH)_2]Br$ (where Py = C_5NH_5), is prepared by the addition of pyridine or of ammonia to an aqueous solution of the tetra-aquobromide, $[CrPy_2(OH_2)_4]Br_3$ (*loc. cit.*).

Hydroxylotriaquodipyridinechromium thiocyanate,

$$[CrPy_2(OH_2)_3(OH)](SCN)_2,$$

prepared from ammonium thiocyanate and tetra-aquodipyridinechromium chloride, forms violet-red crystals; its aqueous solution is greyish-green.

Hydroxylotriaquodipyridinechromium sulphate,

$$[CrPy_2(OH_2)_3(OH)]SO_4,$$

prepared by the addition of pyridine or of ammonia to an aqueous solution of the hydrogen sulphate, $[CrPy_2(OH_2)_4](SO_4)_2H$, forms a green solution with an excess of water.

Dihydroxylodiaquodipyridinechromium sulphate,

$$[CrPy_2(OH_2)_2(OH)_2]_2SO_4,12—14H_2O,$$

prepared by the action of ammonia on tetra-aquodipyridinechromium sulphate, forms greyish-violet crystals. It may also be formed from the trihydroxylo-compound by the careful addition of sulphuric acid. When sulphuric acid is added in excess to dihydroxylodiaquodipyridinechromium sulphate, the latter is converted into the monohydroxylosulphate, which then passes into the hydrogen tetra-aquosulphate. When an aqueous solution of dihydroxylodiaquodipyridinechromium sulphate is decomposed by ammonia, the trihydroxylo-compound is formed.

Chromiumtrihydroxyloaquodipyridine, $[CrPy_2(OH_2)(OH)_3],6H_2O$, prepared by the action of concentrated ammonia on the dihydroxylosulphate or by the action of concentrated ammonia on the monohydroxylosulphate, or by the action of ammonia on a mixture of the dihydroxylochloride and the dihydroxylobromide suspended in water, forms glistening, violet crystals and is insoluble in water. It forms red solutions with dilute mineral acids.

The corresponding dihydroxylo-salts are produced by the action of a little hydrochloric, hydrobromic, or sulphuric acid on an aqueous emulsion of the trihydroxyl compound in question. By the action of an excess of concentrated hydrochloric acid on the trihydroxyl compound, tetra-aquodipyridinechromium chloride is formed. Chromiumtrihydroxyloaquodipyridine is very unstable, undergoing partial decomposition when exposed to air at the ordinary temperature. A green residue is left when the compound is exposed in a desiccator containing phosphoric oxide or when it is kept under diminished pressure, water and pyridine being evolved in each case.

Chromiumdichlorohydroxyloaquodipyridine, $[CrPy_2(OH_2)(OH)Cl_2]$, was prepared as follows. The green product obtained by heating tetra-aquodipyridinechromium chloride in a sealed tube (compare succeeding abstract) was triturated with dilute hydrochloric acid, and to the solution remaining after filtration from chromiumtrichloroaquodipyridine pyridine was probably added, when chromiumdichlorohydroxyloaquodipyridine was precipitated. It is a green microcrystalline powder which decomposes on prolonged exposure to the air at the ordinary temperature and is insoluble in water. Its solutions in dilute mineral acids are green. When suspended in water and ammonia then added, it forms the *compound*, $[CrPy_2(OH_2)_2(OH)_2]Cl$, which, by the action of concentrated hydrochloric acid, is converted into tetra-aquodipyridinechromium chloride, $[CrPy_2(OH_2)_4]Cl_3,2H_2O$.

The constitution of the substances enumerated is discussed. The hydroxy-groupings are directly attached to the chromium atom. The compounds described form salts with acids by direct addition and not by substitution. A. McK.

Hydrate Isomerism with Chromium Salts.

Paul Pfeiffer [and M. Tapuach] (*Ber.*, 1906, 38, 1879—1896).—When the violet-red tetra-aquodipyridinechromium bromide, $[CrPy_2(OH_2)_4]Br_3,2H_2O$, where $Py = C_5NH_5$ (compare Abstr., 1902, i, 728), is allowed to remain for several weeks in a closed vessel, it assumes a green tint. When heated in a closed vessel for three hours at 60—65°, it is converted into the green isomeride, *dibromodiaquodipyridinechromium bromide*,

$$[CrPy_2(OH_2)_2Br_2]Br,4H_2O\,;$$

the latter forms a green solution with ethyl alcohol or methyl alcohol. As distinguished from the violet-red isomeride, it does not form a clear solution with water, since it undergoes hydrolytic dissociation with the separation of a green powder (possibly $[CrPy_2(OH_2)(OH)Br_2]$). When an excess of pyridine is added to a solution of the dibromobromide in water containing hydrochloric acid, a green precipitate of the pseudobase, $[CrPy_2(OH_2)(OH)Br_2]$, is formed; the latter is very labile and is quickly transformed into the basic bromide of the tetra-aquo-series.

Dibromodiaquodipyridinechromium nitrate,
$[CrPy_2(OH_2)_2Br_2]NO_3,4H_2O$,
prepared from nitric acid and dibromodiaquodipyridinechromium bromide, forms dark green needles. It does not form a clear solution with water owing to partial separation of the hydroxylodibromo-compound, which can be dissolved by the addition of mineral acid. When the dibromo-nitrate is added to water, the concentration of bromine ions in the solution remaining after filtration of the hydroxylodibromo-compound is slight. The compound $[CrPy_2(OH_2)_2Br_2]NO_3\ 2H_2O$ may also be obtained as a bright green, microcrystalline powder by varying the conditions of the interaction between nitric acid and dibromodiaquodipyridinechromium bromide.

Dibromodiaquodipyridinechromium iodide, $[CrPy_2(OH_2)_2Br_2]I,4H_2O$, prepared by the addition of ammonium iodide to a solution of dibromodiaquodipyridinechromium bromide in hydrochloric acid, separates in dark green needles; its aqueous solution is turbid, on account of the formation by hydrolytic dissociation of a precipitate, probably consisting of the compound $[CrPy_2(OH_2)(OH)Br_2]$; the solution in dilute acids is green. When the salt is heated, iodine is evolved.

Chromium trichloroaquodipyridine, $[CrPy_2(OH_2)Cl_3],H_2O$, prepared by heating the violet-red variety of tetra-aquopyridine chromium chloride, $[CrPy_2(OH_2)_4]Cl_3,2H_2O$, at 75°, and then washing the residue with hydrochloric acid until the filtrate is no longer green, is a yellowish-green powder. In the aqueous solution of the compound, the chlorine is not in the ionic form. When agitated with water and pyridine, the compound is transformed into the greyish-green dihydroxylochloride,
$[CrPy_2(OH_2)_2(OH)_2]Cl$.
It may also be transformed into the isomeric dichloro-chloride,
$[CrPy_2(OH_2)_2Cl_2]Cl$.

Dichlorodiaquodipyridinechromium chloride pyridinium chloride,
$[CrPy_2(OH_2)_2Cl_2]Cl,HClPy$,
obtained as a by-product in the preparation of chromiumtrichloroaquodipyridine, forms glistening, green needles.

Dichlorodiaquodipyridinechromium chloride, $[CrPy_2(OH_2)_2Cl_2]Cl$, prepared by the action of concentrated hydrochloric acid on chromiumdichlorohydroxyloaquodipyridine (compare preceding abstract), forms glistening, green leaflets; it undergoes hydrolytic dissociation with formation of chromiumdichlorohydroxyloaquodipyridine. When exposed at the ordinary temperature, the crystals lose their lustre and hydrogen chloride is evolved.

Dichlorodiaquodipyridinechromium nitrate,
$[CrPy_2(OH_2)_2Cl_2]NO_3,2H_2O$,
prepared by the action of concentrated nitric acid on chromiumdichlorohydroxyloaquodipyridine, forms green needles. In the aqueous solution of the compound, the chlorine is not in the ionic condition.

Dichlorodiaquodipyridinechromium bromide, $[CrPy_2(OH_2)_2Cl_2]Br,3H_2O$, prepared by the action of hydrobromic acid on chromiumdichlorohydroxyloaquodipyridine, forms dark green, prismatic needles.

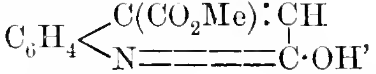
The constitution of these compounds, which are interesting types of isomerism, comparable with Werner's chromium bromide hexahydrates, $[Cr(OH_2)_6]Br_3$ and $[Cr(OH_2)_4Br_2]Br,2H_2O$, is discussed in the preface.

A. McK.

Preparation of Indoxyl and its Homologues. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 166213, 166214).—A mixture of potassium phenylglycinate, sodium and potassium hydroxides, and magnesium nitride is heated at 220—270° until the fused mass assumes a deep orange or brown colour. The product, when dissolved in water, filtered from magnesium hydroxide, and oxidised, gives a good yield of indigotin.

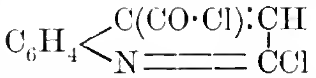
The phenylglycine employed in this reaction may be replaced by one of its homologues, and any other nitride of the alkaline earths may be substituted for the magnesium compound. A similar result is obtained when calcium carbide or any other alkali or alkaline-earth carbide is employed instead of the nitride. G. T. M.

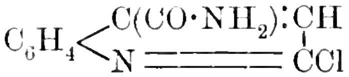
3-Ethylcinchonic Acid and 2-Hydroxy-3-ethylcinchonic Acid. B. Mulert (*Ber.*, 1906, 39, 1901—1908. Compare Hübner, this vol., i, 383).—*Methyl 2-hydroxycinchonate,*

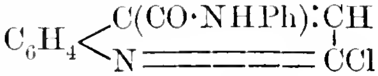


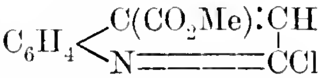
$$C_6H_4<\begin{array}{ll}C(CO_2Me){:} & CH\\ N{=\!=\!=\!=\!=\!=} & C{\cdot}OH\end{array}$$

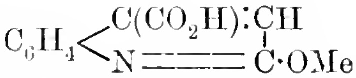
prepared by the action of hydrogen chloride on a solution of 2-hydroxycinchonic acid in methyl alcohol, melts at 245°. The corresponding *amide,*  $C_6H_4<\begin{array}{ll}C(CO{\cdot}NH_2){:} & CH\\ N{=\!=\!=\!=\!=} & C{\cdot}OH\end{array}$, melts at 357—358°.

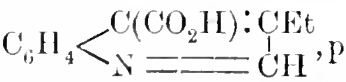
2-*Chlorocinchonyl chloride,*  $C_6H_4<\begin{array}{ll}C(CO{\cdot}Cl){:} & CH\\ N{=\!=\!=\!=} & CCl\end{array}$, prepared by the action of thionyl chloride on 2-hydroxycinchonic acid, melts at 89—90° and is very stable towards cold water.

2-*Chlorocinchonamide,*  $C_6H_4<\begin{array}{ll}C(CO{\cdot}NH_2){:} & CH\\ N{=\!=\!=\!=\!=} & CCl\end{array}$, separates from dilute alcohol in prismatic needles and melts at 234—235°; on further heating it solidifies and again melts at 276—278°.

2-*Chlorocinchonanilide,*  $C_6H_4<\begin{array}{ll}C(CO{\cdot}NHPh){:} & CH\\ N{=\!=\!=\!=\!=\!=} & CCl\end{array}$, separates from alcohol in needles and melts at 202°.

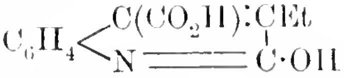
Methyl 2-chlorocinchonate,  $C_6H_4<\begin{array}{ll}C(CO_2Me){:} & CH\\ N{=\!=\!=\!=\!=} & CCl\end{array}$, prepared by the addition of 2-chlorocinchonyl chloride to methyl alcohol, melts at 89—90°.

2-*Methoxycinchonic acid,*  $C_6H_4<\begin{array}{ll}C(CO_2H){:} & CH\\ N{=\!=\!=\!=} & C{\cdot}OMe\end{array}$, prepared by the action of sodium methoxide on 2-chlorocinchonic acid, separates from benzene in needles and melts at 178—179°. When heated above its melting point, it is transformed into the isomeric methyl 2-hydroxycinchonate melting at 245—255°. Its *methyl* ester separates from alcohol in needles and melts at 71°.

3-*Ethylcinchonic acid,*  $C_6H_4<\begin{array}{ll}C(CO_2H){:} & CEt\\ N{=\!=\!=\!=} & CH\end{array}$, prepared by the condensation of isatin with butaldoxime in the presence of potassium hydroxide, melts at 222°. Its *sodium* and *silver* salts and its *platinichloride* were prepared. Its *methyl betaine*, $C_{13}H_{13}O_2N$, prepared by the action of methyl iodide on the silver salt, crystallises in needles and melts at 261°.

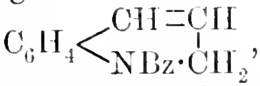
3-*Ethylcinchonic chloride hydrochloride*, $C_{12}H_{10}ONCl,HCl$, crystallises in needles and melts at 174—175°.

The *amide*, $C_{12}H_{12}ON_2$, separates from water in needles and melts at 220—221°. The *methyl* ester, $C_{13}H_{13}O_2N$, separates from ether in hexagonal prisms and melts at 37—38°.

2-*Hydroxy-3-ethylcinchonic acid*,  $C_6H_4<\begin{matrix}C(CO_2H){:}CEt\\ N{=\!=\!=}C\cdot OH\end{matrix}$, prepared from isatin and butyric anhydride in presence of aqueous sodium hydroxide, crystallises from water in needles and melts at 285°. Its *sodium* and *silver* salts are described. Its *acid chloride*, prepared by the action of thionyl chloride, separates from chloroform in plates and melts at 194—195°. Its *methyl* ester melts at 160°; its *amide* melts at 304—305°.

A. McK.

Synthesis in Sunlight. ALFRED BENRATH (*J. pr. Chem.*, 1906, [ii], 73, 383—389. Compare Klinger and Standke, Abstr., 1891, 900; Klinger and Kolvenbach, Abstr., 1898, i, 467).—When mixed with *iso*butaldehyde, salicylaldehyde, or benzaldehyde, and exposed to sunlight, benzil is reduced to benzilbenzoin; anisaldehyde has only a slight, whilst furfuraldehyde, cinnamaldehyde, and valeraldehyde have no reducing action on benzil in sunlight.

1-*Benzoyl*-1 : 2-*dihydroquinoline*,  $C_6H_4<\begin{matrix}CH{:}CH\\ NBz\cdot CH_2\end{matrix}$, is formed when benzaldehyde and quinoline are exposed to sunlight; it crystallises in slender, white needles, melts at 200°, is not a base, and is hydrolysed by concentrated hydrochloric acid, forming benzoic acid and 1 : 2-dihydroquinoline (?); if it is hydrolysed with a hot alkali hydroxide solution, the resulting base is oxidised to quinoline.

2-β-Hydroxy-β-phenylethylquinoline,

$$C_6H_4<\begin{matrix}CH{:}CH\\ N{=}C\cdot CH_2\cdot CHPh\cdot OH\end{matrix},$$

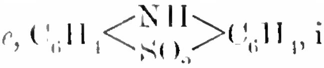
formed in the same manner from benzaldehyde and 2-methylquinoline, crystallises from alcohol, melts at 131°, decomposes when heated, forming 2-styrylquinoline, water, 2-methylquinoline, and benzaldehyde, and when boiled with acetic anhydride yields 2-styrylquinoline. The *salts* are only sparingly soluble; the *nitrate* crystallises in yellow, feathery aggregates and melts at 153°; the *platinichloride*, $(C_{17}H_{15}ON)_2,H_2PtCl_6$, melts at 232°.

The action of benzaldehyde on cinnamic acid in sunlight leads to the formation of $\alpha\delta$-dibenzoyl-$\beta\gamma$-diphenylbutane.

Benzaldehyde and pyridine do not interact when exposed to sunlight.

G. Y.

Chemical Nature of Methylene-azure. AUGUST BERNTHSEN (*Ber.*, 1906, 39, 1804—1809).—The author discusses the constitution of methylene-azure, and confirms Kehrmann's discovery that this substance is a mixture of di- and tri-methylthionine (this vol., i, 460).

Diphenylaminesulphone,  $C_6H_4{<}\genfrac{}{}{0pt}{}{NH}{SO_2}{>}C_6H_4$, is produced when methyldiphenylaminesulphone is heated with hydriodic acid, methyl iodide being formed quantitatively. It crystallises in long needles and melts at 257—259°. C. S.

Condensation Products of Rhodanic Acid with Aldehydes.

Guido Bargellini (*Atti R. Accad. Lincei*, 1906, [v], **15**, i, 181—185. Compare this vol., i, 383).—Reduction of *o*-nitrobenzylidenerhodanic acid (Bondzyński, Abstr., 1887, 1108) by means of ferrous sulphate in ammoniacal solution yields o-*aminobenzylidenerhodanic acid*, which is deposited from aqueous alcohol in blood-red crystals, turning yellow at 200 and decomposing at 265—269°.

m-*Nitrobenzylidenerhodanic acid*,  $NO_2\cdot C_6H_4\cdot CH{:}C{<}\begin{smallmatrix}S-CS\\ \ \ \ \ \ |\\ CO\cdot NH\end{smallmatrix}$, prepared by the action of concentrated sulphuric acid on an alcoholic solution of rhodanic acid and *m*-nitrobenzaldehyde, crystallises from acetic acid in lemon-yellow needles melting and decomposing at 255° and is moderately soluble in benzene, ether, or chloroform, and readily so in alcohol, ethyl acetate, or acetone.

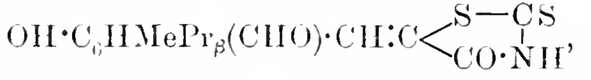
p-Dimethylaminobenzylidenerhodanic acid crystallises from alcohol in minute, blood-red needles, which begin to melt at 240° and are completely melted at about 270° (compare Andreasch and Zipser, Abstr., 1905, i, 930).

p-iso*Propylbenzylidenerhodanic acid*, $C_{13}H_{13}ONS_2$, prepared from cuminaldehyde and rhodanic acid, crystallises from aqueous alcohol in red needles melting at 154—157°, and is moderately soluble in benzene or ether and readily so in chloroform, acetic acid, or acetone.

4-*Hydroxy*-2-*methyl*-5-iso*propylbenzylidenerhodanic acid*,

$$C_{14}H_{15}O_2NS_2,$$

prepared from thymotic aldehyde and rhodanic acid, forms a mass of orange, woolly crystals melting at 220—221°, and dissolves readily in alcohol, ether, ethyl acetate, acetic acid, or acetone, and to a slight extent in benzene or chloroform.

Thymotic dialdehyde and rhodanic acid give the condensation *product*,  $OH\cdot C_6HMePr_\beta(CHO)\cdot CH{:}C{<}\begin{smallmatrix}S-CS\\ \ \ \ \ \ |\\ CO\cdot NH\end{smallmatrix}$, which crystallises from alcohol in yellow needles melting at 239—240° and is soluble in ether, ethyl acetate, acetone, or acetic acid, and to a slight extent in benzene.

β-Hydroxynaphthaldehyde and rhodanic acid yield the *compound*  $OH\cdot C_{10}H_6\cdot CH{:}C{<}\begin{smallmatrix}S-CS\\ \ \ \ \ \ |\\ CO\cdot NH\end{smallmatrix}$, which crystallises from aqueous alcohol in dark chestnut-red needles blackening at 210° and melting and decomposing at 220°, and dissolves readily in ether, benzene, chloroform, acetone, or acetic acid. T. H. P.

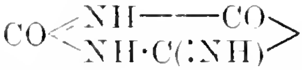
4 : 5-Diamino-2 : 6-dihydroxy-3-methylpyrimidine.

Emanuel Merck (D.R.-P. 166267).—4 : 5-*Diamino*-2 : 6-*dihydroxy*-3-*methylpyrimidine* is readily obtained by dissolving 5-*iso*nitroso-4-amino-2 : 6-

dihydroxy-3-methylpyrimidine in 60 per cent. sulphuric acid and electrolysing the solution in the cathode cell with leaden cathode and a current density of 3 amperes per sq. dm. The liquid is finally saturated with ammonia, when the diamine is set free in a very pure condition. G. T. M.

Preparation of Cyclic Carbamide Derivatives (Pyrimidines).

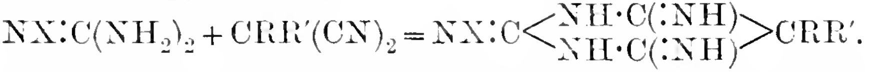
EMANUEL MERCK (D.R.-P. 165561 and 165562).—Carbamide and its alkyl derivatives can be converted into pyrimidine bases by treatment with ethyl cyanoacetate in the presence of an alkali metal or its ethoxide or amide.

4-Amino-2 : 6-dioxypyrimidine,  $CO\left<\begin{array}{l}NH\text{——}CO\\NH\cdot C(:NH)\end{array}\right>CH_2$, is prepared by the interaction of carbamide, sodamide, and ethyl cyanoacetate in xylene solution.

4-*Ethylamino*-2 : 6-*dioxypyrimidine*, obtained by condensing ethyl carbamide and ethyl cyanoacetate in the presence of sodium ethoxide, crystallises in fine needles and possesses both basic and acidic properties. The is*onitroso*-derivative of this base is a well-defined, violet-red substance melting indefinitely at 278—280°. G. T. M.

Preparation of Derivatives of Barbituric Acid.

EMANUEL MERCK (D.R.-P. 165692 and 165693).—Malononitrile and its mono- and di-*C*-alkylated homologues and guanidine and its derivatives undergo condensation to yield derivatives of tri-iminobarbituric acid (2 : 4 : 6-tri-iminopyrimidine),



$$NX{:}C(NH_2)_2 + CRR'(CN)_2 = NX{:}C\left<\begin{array}{l}NH\cdot C(:NH)\\NH\cdot C(:NH)\end{array}\right>CRR'.$$

These pyrimidine derivatives are readily hydrolysed to the corresponding barbituric acids, which have a distinctly soporific action.

2 : 4 : 6-*Tri-iminopyrimidine*, melting at 252°, obtained from malononitrile and guanidine in alcoholic solution, yields sparingly soluble salts with the mineral acids and forms a violet nitroso-derivative. The *compound* from guanidine and ethylmalononitrile melts at 190°. 2 : 4 : 6-*Tri-imino*-5 : 5-*diethylpyrimidine* melts at 240° and has a strongly alkaline reaction. The *compound* from methylguanidine and diethylmalononitrile forms cubical crystals and melts at 172°. The *compound* $C_9H_{14}N_6$, obtained from diethylmalononitrile and either dicyanodiamide or diguanide, melts at 183°.

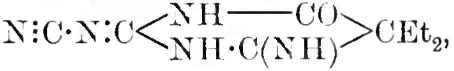
4 : 6-*Di-imino*-2-*oxy*-5-*diethylpyrimidine*, melting at 272°, obtained from carbamide and diethylmalononitrile, when boiled with 30 per cent. sulphuric acid yields diethylbarbituric acid. This substance may also be prepared from 2 : 4 : 6-tri-imino-5 : 5-diethylpyrimidine, melting at 240°, obtained by condensing diethylmalononitrile with guanidine.

Ethylbarbituric acid (m. p. 194°) is prepared from 2 : 4 : 6-*tri-imino*-5-*ethylpyrimidine*, melting at 190°, and propylbarbituric acid may be produced from 4 : 6-*di-imino*-2-*oxy*-5-*propylpyrimidine*, which decomposes at 300° and is prepared from propylmalononitrile and carbamide in the presence of boiling alcoholic sodium ethoxide. G. T. M.

Preparation of 5 : 5-Dialkylbarbituric Acids. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 165223).—By the action of dicyanodiamide on dialkylated cyanoacetates, malonates, or dialkylmalononitriles in the presence of alkaline condensing agents, pyrimidine derivatives are produced having the following general formula, $N{:}C{\cdot}N{:}C{<}\begin{matrix}NH{\cdot}C({:}X)\\NH{\cdot}C({:}X)\end{matrix}{>}CR_2$, where R represents alkyl groups and X signifies oxygen atoms or imino-groups. These substances on treatment with acids furnish the corresponding substituted barbituric acids,

$$CO{<}\begin{matrix}NH{\cdot}CO\\NH{\cdot}CO\end{matrix}{>}CR_2.$$

Iminocyanoimino-oxydiethylpyrimidine,

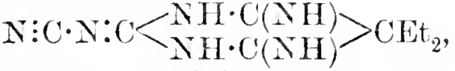


$$N{:}C{\cdot}N{:}C{<}\begin{matrix}NH\text{——}CO\\NH{\cdot}C(NH)\end{matrix}{>}CEt_2,$$

prepared from dicyanodiamide and ethyl diethylcyanoacetate in presence of an alkali ethoxide, separates from water in needles melting at 265° and yields diethylbarbituric acid on boiling with 20 per cent. sulphuric or oxalic acid.

Cyanoiminodioxydiethylpyrimidine, $N{:}C{\cdot}N{:}C{<}\begin{matrix}NH{\cdot}CO\\NH{\cdot}CO\end{matrix}{>}CEt_2$, from dicyanodiamide, ethyl diethylmalonate, and alkali ethoxide, melts at 242° and is readily hydrolysed by 25 per cent. hydrochloric acid.

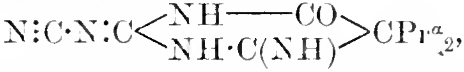
Di-iminocyanoiminodiethylpyrimidine,



$$N{:}C{\cdot}N{:}C{<}\begin{matrix}NH{\cdot}C(NH)\\NH{\cdot}C(NH)\end{matrix}{>}CEt_2,$$

obtained from dicyanodiamide and diethylmalononitrile, melts at 270°.

Iminocyanoimino-oxydiethylpyrimidine,



$$N{:}C{\cdot}N{:}C{<}\begin{matrix}NH\text{——}CO\\NH{\cdot}C(NH)\end{matrix}{>}CPr^{a}_{2},$$

arising from ethyl dipropylcyanoacetate, melts at 272°, and when hydrolysed with 25 per cent. hydrobromic acid yields 5 : 5-dipropylbarbituric acid. G. T. M.

Preparation of 5 : 5-Dialkylbarbituric Acids. ALFRED EINHORN (D.R.-P. 165649).—The 5 : 5-dialkylbarbituric acids may be obtained from the corresponding thiobarbituric acids by heating with non-oxidising mineral acids. After six to seven hours' boiling with concentrated hydrobromic acid or 33—50 per cent. sulphuric acid, diethylthiobarbituric acid is hydrolysed and dissolved, and pure 5 : 5-diethylbarbituric acid may be isolated from the product. Hydriodic, hydrochloric, sulphurous, and phosphoric acids may also be employed, and the hydrolysis is accelerated by the addition of alcohol. G. T. M.

Preparation of 2-Arylimino- and 2-Arylhydrazino-5 : 5-dialkylbarbituric Acids. ALFRED EINHORN (D.R.-P. 166266).—When the thiodialkylbarbituric acids are heated with aromatic amines, sulphur is displaced by the amino-residues and aryliminodialkylbarbituric acids are obtained.

2-*Phenyliminodiethylbarbituric acid*, which results from the interaction of aniline and thiodiethylbarbituric acid at 120—130°, crystallises from alcohol in white needles or leaflets melting at 253° ; when boiled with mineral acids, it is hydrolysed, yielding aniline and diethylbarbituric acid.

2-*Phenylhydrazinodiethylbarbituric acid*, obtained under similar conditions from thiodiethylbarbituric acid and phenylhydrazine, is sparingly soluble in methyl and ethyl alcohols, crystallising from the former in yellow leaflets melting at 215—216°; it dissolves in dilute aqueous sodium hydroxide, and the solution passes through a series of colour changes—brown, reddish-brown, deep violet, and finally brown again; the liquid at the same time gradually becomes turbid. This hydrazino-derivative is hydrolysed by concentrated mineral acids, phenylhydrazine being eliminated.

2-*Phenyliminodimethylbarbituric acid* crystallises from alcohol in needles melting at 251°. G. T. M.

Affinity Constants of Cyclic Bases. GEORG DEDICHEN (*Ber.*, 1906, **39**, 1831—1856).—The dissociation constants have been determined of substituted glyoxalines by the conductivity method, of derivatives of pyrazole, triazole, and of *iso*dihydrotetrazine by Lowenherz's solubility process, or by the hydrolysis of ethyl formate.

The original paper must be consulted for the tabulated results. In general, the introduction of the methyl or ethyl group affects the affinity of the base to approximately the same extent. The position of the alkyl group has a very marked influence; when it is attached to a nitrogen atom, the effect on the dissociation constant is small, but the affinity of the base is largely increased when an alkyl group is combined with carbon. The introduction of a chlorine atom into 1-methylglyoxaline greatly diminishes the value of K. C. S.

Resolution of the Iminazole and Oxazole Rings. OTTO FISCHER (*J. pr. Chem.*, 1906, [ii], **73**, 419—446. Compare Abstr., 1905, i, 245).—[With FRITZ RÖMER.]—1-Methyl-, 1-ethyl-, and 1-phenylbenziminazoles are not reduced by sodium and alcohol.

The action of methyl iodide on 2 : 5-dimethylbenziminazole leads to the formation of 1 : 2 : 3 : 6-tetramethylbenziminazolium iodide and the hydriodides of 1 : 2 : 5- and 1 : 2 : 6-trimethylbenziminazoles (Fischer and Rigaud, Abstr., 1902, i, 399).

1 : 2 : 3 : 6-Tetramethyl-2 : 3-dihydrobenziminazole-2-ol (Fischer and Rigaud, *loc. cit.*) sublimes and decomposes only slightly when carefully heated, but decomposes to a marked extent when rapidly heated or distilled. It crystallises from light petroleum in sheaves of needles melting at 148—150°, or from water or very dilute alcohol in plates melting at 166—167°, and distils only slowly in a current of steam. It dissolves in cold acids, and can be reprecipitated immediately by alkali hydroxides or ammonia, but in the acid solution gradually changes into the benziminazolium salt, and is no longer precipitated by ammonia. 1 : 2 : 3 : 6-Tetramethylbenziminazolium picrate melts at 147—148° (compare Niementowski, Abstr., 1887, 937). The *nitrosoamine*, $NO\cdot NMe\cdot C_6H_4Me\cdot NMeAc$, is formed by the action of sodium nitrite on 1 : 2 : 3 : 6-tetramethyldihydrobenziminazole-2-ol in concentrated sulphuric acid solution at 0° : it crystallises from a mixture of alcohol and light petroleum in long, stout, colourless prisms, melts

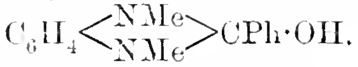
at 71°, becomes yellow or brown in presence of moisture, and gives Liebermann's reaction. The action of alcoholic hydrochloric acid on the nitrosoamine in ethereal solution leads to the formation of 1 : 2 : 3 : 6-tetramethylbenziminazolium chloride.

When heated with sodium hydroxide in alcoholic solution in a sealed tube at 150°, the carbinol or 1 : 2 : 3 : 6-tetramethylbenziminazolium iodide is decomposed, forming 3 : 4-dimethylaminotoluene, the hydrochloride of which has the formula $C_9H_{16}N_2Cl_2$ (compare Fischer and Rigaud, *loc. cit.*).

The reduction of the carbinol with sodium and alcohol or zinc dust in alkaline solution leads to the formation of 1 : 2 : 3 : 6-*tetramethyl-2 : 3-dihydrobenziminazole*,  $C_6H_3Me{<}\begin{matrix}NMe\\NMe\end{matrix}{>}CHMe$, which is readily hydrolysed, yielding acetaldehyde and 3 : 4-dimethylaminotoluene.

When reduced with sodium and alcohol, 1 : 3 : 4 : 6-tetramethyldihydrobenziminazole-2-ol yields formaldehyde and m-*xylylene*-4 : 5-*dimethyldiamine*, $C_6H_2Me_2(NHMe)_2$. This is obtained as an oil, which boils at 245—250° under 730 mm. pressure, gives with ferric chloride in dilute solution a brownish-red coloration, or in concentrated hydrochloric acid solution a yellow *ferrichloride*, gradually changing into the red *azine* dye, and reacts with formic acid to form 1 : 3 : 4 : 6-tetramethyldihydrobenziminazole-2-ol, or with aldehydes to form unstable dihydrobenziminazoles. The *hydrochloride*, $C_{10}H_{16}N_2,2HCl$, crystallises in white, flat prisms. When mixed with salicylaldehyde, the base forms water, and the *condensation product*, $C_{17}H_{20}ON_2$, which crystallises from ether in colourless plates, melts at 132—133° and is hydrolysed to salicylaldehyde and the *o*-diamine when boiled with acids.

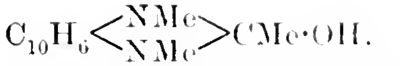
2-*Phenyl*-1 : 3-*dimethylbenziminazolium iodide*, $C_{15}H_{15}N_2I$, formed by heating 2-phenylbenziminazole with methyl iodide and methyl alcohol in a sealed tube at 110°, crystallises in white needles, melts at 278—279°, and, when treated with a hot aqueous alkali hydroxide, forms 2-*phenyl*-1 : 3-*dimethyl*-2 : 3-*dihydrobenziminazole-2-ol*,



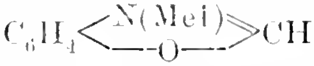
$$C_6H_4{<}\begin{matrix}NMe\\NMe\end{matrix}{>}CPh\cdot OH.$$

This crystallises in white, tetragonal prisms, melts at 159°, forms a *ferrichloride*, which is readily soluble in water, and with hydriodic acid yields the above benziminazolium iodide, or with alcoholic hydrochloric acid the *chloride*, $C_{15}H_{15}N_2Cl$. When dissolved in dilute hydrochloric acid, cooled by ice, and immediately treated with ammonia, 2-phenyl-1 : 3-dimethyldihydrobenziminazole-2-ol is regained unchanged, but after twenty to thirty minutes in the acid solution it is converted into the benziminazolium salt, which does not give a precipitate with ammonia. The *picrate* of the carbinol melts at 157—158°. When boiled with alcoholic potassium hydroxide, the carbinol is decomposed and forms *o*-phenylenedimethyldiamine.

2-Methyl-α-naphthiminazole melts at 171—172° (168—169°; Abstr., 1901, i, 414); when heated with methyl iodide and methyl alcohol in a sealed tube at 140—145°, it forms 1 : 2 : 3-*trimethyl-α-naphthiminazolium iodide*, $C_{14}H_{15}N_2I$, which crystallises in voluminous, white needles, becomes red when dried, melts at 294°, and when treated with aqueous-alcoholic potassium hydroxide yields the *carbinol*,

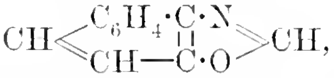

$C_{10}H_6<\begin{matrix}NMe\\NMe\end{matrix}>CMe\cdot OH$. This crystallises in white, tetragonal prisms, is readily soluble in alcohol, ether, or benzene, forming a solution with violet fluorescence, yields a yellow, crystalline *ferrichloride*, and is converted by acids slowly into the naphthiminazolium salts. The carbinol is very stable towards hydrolysing agents, remaining unchanged when heated with 50 per cent. alcoholic potassium hydroxide at 140—150°, and does not form an azine dye when treated with ferric chloride. The *nitrosoamine*, which is obtained in small yields when the carbinol is treated with sodium nitrite and dilute sulphuric acid cooled by ice, crystallises in slightly yellow plates, melts at 134—135°, and gives Liebermann's reaction.

When heated with methyl iodide and methyl alcohol at 120° in a sealed tube, benzoxazole forms *o*-trimethylaminophenol iodide (Griess, Abstr., 1880, 636). *Benzoxazole methiodide*,


$C_6H_4<\begin{matrix}N(MeI)\\O\end{matrix}>CH$, is formed when benzoxazole is heated with an excess of methyl iodide, without methyl alcohol, in a sealed tube at 100°; it crystallises in glistening, yellow needles, melts and evolves iodine at 182—183°, and decomposes when exposed to sunlight. When boiled with concentrated hydrochloric acid, the methiodide is hydrolysed, forming *o*-methylaminophenol.

When heated with methyl iodide at 170°, 2-phenylbenzoxazole yields only a small amount of an impure product containing iodine. Contrary to Hübner's statement (Abstr., 1882, 505), the product of the nitration of 2-phenylbenzoxazole is a *mononitro*-derivative, which, when hydrolysed with concentrated hydrochloric acid, yields benzoic acid. The *picrate*, $C_{13}H_9ON,C_6H_3O_7N_3$, crystallises in matted, yellow needles and melts at 104°.

a-Naphthoxazole,


$CH<\begin{matrix}C_6H_4\cdot C\cdot N\\ \| \\ CH—C\cdot O\end{matrix}>CH$, is prepared by heating *a*-amino-*β*-naphthol hydrochloride with sodium formate and formic acid in a reflux apparatus; it crystallises in white leaflets, melts at 63·5—64°, and is partially hydrolysed when heated with an aqueous alkali hydroxide. The *platinichloride* is unstable; the *mercurichloride*, $C_{11}H_7ON,HgCl_2$, crystallises in long, colourless, glistening needles and melts at 183—184°; the *picrate*, $C_{11}H_7ON,C_6H_3O_7N_3$, forms needles and melts at 133—134°. The *mononitro*-product, $C_{11}H_6O_3N_2$, formed by the action of cold nitric and sulphuric acids on *a*-naphthoxazole, crystallises in brownish-yellow needles and melts at 135°. When boiled with water in a reflux apparatus for four hours, *a*-naphthoxazole is hydrolysed, yielding *a-formylamino-β-naphthol*,

$$OH\cdot C_{10}H_6\cdot NH\cdot COH,$$

which crystallises in white, prismatic needles, melts at 204°, and is hydrolysed by boiling concentrated alkali hydroxides, yielding ammonia and *aβ*-dihydroxynaphthalene. When oxidised with chromic acid in glacial acetic acid solution, *a*-naphthoxazole yields a small amount of an *o*-dicarboxylic acid.

β-Naphthoxazole, $C_{11}H_7ON$, prepared from *β*-amino-*a*-naphthol, crystallises in stellate groups of slender needles, melts at 79° and is hydrolysed to only a slight extent by boiling water. When boiled with dilute hydrochloric acid, it is decomposed, forming iminooxydihydronaphthalene on saturating the solution with ammonia. When boiled with dilute potassium hydroxide, it yields ammonia and $\alpha\beta$-dihydroxynaphthalene.

Triphenylglyoxaline [lophine], when heated with methyl iodide and methyl alcohol at 120—130°, forms *triphenyldimethylglyoxalinium iodide*, $C_{23}H_{21}N_2I$, which separates from alcohol in white crystals, melts at 266°, and remains unchanged when treated with alcoholic potassium hydroxide. When reduced with sodium and alcohol, it yields benzoic acid, methylamine, and *s-dimethylstilbenediamine*, $C_{16}H_{20}N_2$, which is formed also by hydrolysis of *i*-benzoyl-*s*-dimethylstilbenediamine (Japp and Moir, Trans., 1900, **77**, 608) with concentrated hydrochloric acid at 170—180°. The *hydrochloride* of the diamine, $C_{16}H_{20}N_2,2HCl$, was analysed; the *aurichloride*, *platinichloride*, *mercurichloride*, and *picrate* are crystalline. The *dinitrosoamine*, $C_{16}H_{18}O_2N_4$, crystallises from acetone in almost colourless, tetragonal prisms, melts at 266—267°, and gives Liebermann's reaction.

The *diacetyl* derivative, $C_{20}H_{24}O_2N_2$, crystallises in white, nodular aggregates and melts at 250—251°. The *dibenzoyl* derivative, $C_{30}H_{28}O_2N_2$, melts at 248—250°.

The *nitroso*-derivative of *i*-benzoyl-*s*-dimethylstilbenediamine melts at 213—215°, and gives Liebermann's reaction. G. Y.

Preparation of Indoxyl and its Derivatives. BASLER CHEMISCHE FABRIK (D.R.-P. 165691).

—A convenient process for obtaining indoxyl from phenylglycine consists in adding the potassium salt of the latter to an intimate mixture of potassium hydroxide and sodium oxide (prepared from the metal) heated at 210—260°. The fused mass from ten parts of the alkali phenylglycine derivative when dissolved in water and oxidised by a current of air yielded 4·8 parts of indigo. In this experiment, the phenylglycine may be replaced by its homologues, giving rise to the corresponding indoxyl derivatives.

G. T. M.

Synthesis of Derivatives of Ketoquinazoline. BRONISLAW VON PAWLEWSKI (*Ber.*, 1906, **39**, 1732—1736. Compare Abstr., 1905, i, 246; Kunckell, Abstr., 1905, i, 382).

—Anthranilic acid reacts with disubstituted carbamides or thiocarbamides to form only monosubstituted derivatives of ketotetrahydroquinazoline, in the sense of the equation $NH_2\cdot C_6H_4\cdot CO_2H + NHR\cdot CO\cdot NHR' =$  $C_6H_4<\begin{matrix}CO-NR\\ NH\cdot CO\end{matrix}$ $+ H_2O + R'NH_2$. Thus, phenylallylthiocarbamide forms 4-keto-2-thion-3-phenyl-1 : 2 : 3 : 4-tetrahydroquinazoline, allylamine, and water.

Molecular quantities of anthranilic acid and allyl thiocarbamide at 150—180° react to form *4-keto-2-thion-3-allyl-1 : 2 : 3 : 4-tetrahydroquinazoline*,  $C_6H_4<\begin{matrix}CO-N\cdot C_3H_5\\ NH\cdot CS\end{matrix}$, which melts at 303—304°, and is oxidised by hydrogen peroxide in alkaline solution to *2 : 4-diketo-3-allyl-1 : 2 : 3 : 4-tetrahydroquinazoline*, which separates from alcohol in needles and melts at 276—278°.

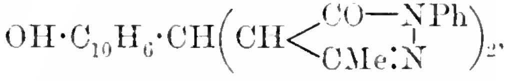
4-*Keto*-2-*thion*-1-*allyl*-1 : 2 : 3 : 4-*tetrahydroquinazoline* is obtained when a mixture of anthranilic acid and allyl thiocarbimide is heated at 160—165° and finally at 170—180°. It crystallises from alcohol in long prisms, melts at 208—210°, and is oxidised by hydrogen peroxide to 2 : 4-*diketo*-1-*allyl*-1 : 2 : 3 : 4-*tetrahydroquinazoline*, which separates from alcohol in long, irregular leaflets and melts at 187—189°.

Anthranilic acid and *o*-tolylthiocarbimide react to form 4-*keto*-2-*thion*-3-o-*tolyl*-1 : 2 : 3 : 4-*tetrahydroquinazoline* (compare MacCoy, Abstr., 1897, i, 490; Freundler, Abstr., 1904, i, 830), which crystallises in colourless prisms and needles, melts at 270—271°, and is oxidised by hydrogen peroxide to Busch's 2 : 4-diketo-3-*o*-tolyl-1 : 2 : 3 : 4-tetrahydroquinazoline (Abstr., 1895, i, 307). C. S.

Preparation of Diaminodinaphthazines. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 166363).—The dinaphthazines when dissolved in concentrated sulphuric acid readily yield dinitro-derivatives on nitration; these products on reduction give rise to diaminodinaphthazines, which furnish valuable azo-colouring matters. These diaminodinaphthazines, unlike the aminoazines already described, which contain the amino-group in the para-position, do not exchange this group for hydroxyl on heating under pressure with hydrochloric acid.

$\alpha\beta$-Dinaphthazine furnishes a *dinitro*-derivative which is very sparingly soluble in all indifferent solvents and crystallises from nitrobenzene in small, yellow needles melting above 300°. This product is reduced to the corresponding *diamino-αβ-dinaphthazine* by mixing intimately with concentrated sodium sulphide solution and heating the mixture at 90—100°. The diamine is a red substance melting above 300°; it is insoluble in water and sparingly soluble in all organic solvents; its *sulphate* separates from aqueous solutions in very sparingly soluble pale yellow crystals. The compounds obtained under these conditions from $\beta\beta$-dinaphthazine are quite analogous to the preceding substances. G. T. M.

Condensation Reaction of the Pyrazolones. Mario Betti and Curio M. Mundici (*Gazzetta*, 1906, 36, i, 178—187).—Pyrazolone reacts with β-hydroxynaphthaldehyde, forming in the first place an unstable, intermediate compound,



$$OH\cdot C_{10}H_6\cdot CH\left(CH<\begin{matrix}CO-NPh\\ CMe:N\end{matrix}\right)_2,$$

which readily decomposes, yielding methenylbisphenylmethylpyrazolone,

$$\begin{matrix}NPh\cdot CO\\ N{=}CMe\end{matrix}>CH\cdot CH:C<\begin{matrix}CO-NPh\\ CMe:N\end{matrix}.$$

The reaction evidently depends on the known tendency of the pyrazolones to form the grouping $=CH\cdot CH:C=$. β-Hydroxynaphthaldehyde does not react with methyl*iso*oxalazone or with partially substituted pyrazolones or with ethyl malonate; with aromatic amines, it yield anilides and hydrazones.

Methylbisphenylmethylpyrazolone, $C_{21}H_{18}O_2N_4$, crystallises in shining, orange-yellow needles melting at 180°, and dissolves moderately well in alcohol and to a slight extent in other organic solvents. It is soluble in sodium hydroxide solution and in concentrated sulphuric acid, to which it imparts an intense yellow colour.

The intermediate compound, *β-hydroxynaphthylidenebisphenylmethylpyrazolone*, $C_{31}H_{26}O_3N_4$, separates in slender, yellow needles melting at 118° to a turbid, yellow liquid which becomes transparent at about 140°; it cannot be purified, owing to its instability.

Methenylbismethylpyrazolone,


$$\begin{matrix}\mathrm{NH{-}CO}\\ |\\ \mathrm{N{=}CMe}\end{matrix}\!>\mathrm{CH\cdot CH{:}C}<\!\begin{matrix}\mathrm{CO{-}NH}\\ |\\ \mathrm{CMe{=}N}\end{matrix},$$

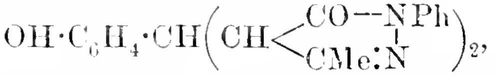
crystallises from alcohol with EtOH in golden-yellow needles melting at 130—140°, and dissolves in concentrated sulphuric acid giving a yellow coloration, and in sodium hydroxide solution forming an intensely yellow liquid.

Methenylbisdiphenylpyrazolone,


$$\begin{matrix}\mathrm{NPh\cdot CO}\\ |\\ \mathrm{N{=}CPh}\end{matrix}\!>\mathrm{CH\cdot CH{:}C}<\!\begin{matrix}\mathrm{CO{-}NPh}\\ |\\ \mathrm{CPh{:}N}\end{matrix},$$

crystallises from alcohol in reddish-yellow needles and from benzene in orange-yellow needles melting at 249—250°.

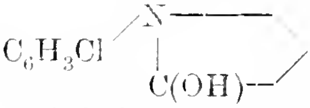
o-*Hydroxybenzylidenebisphenylmethylpyrazolone*,


$$\mathrm{OH\cdot C_6H_4\cdot CH}\left(\mathrm{CH}<\!\begin{matrix}\mathrm{CO{-}NPh}\\ |\\ \mathrm{CMe{:}N}\end{matrix}\right)_2,$$

prepared from salicylaldehyde and phenylmethylpyrazolone, crystallises from alcohol in colourless needles melting at 228—230°, dissolves but slightly in other organic solvents, forms a reddish-yellow solution with concentrated sulphuric acid, and dissolves in sodium hydroxide solution.

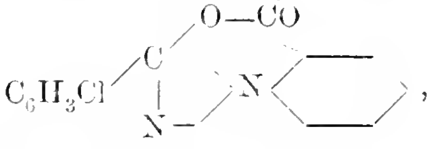
Anisylidenebisphenylmethylpyrazolone, $C_{28}H_{25}O_3N_4$, crystallises from alcohol in colourless needles which contain EtOH and melt at 148°, and dissolves in sodium hydroxide solution or concentrated sulphuric acid. T. H. P.

Azo-compounds. Transformation of *o*-Carboxylic Azo-compounds into 3-Hydroxyindazyl Derivatives. PAUL FREUNDLER (*Compt. rend.*, 1906, **142**, 1153—1155.—Compare Abstr., 1903, i, 371, 585; 1904, i, 121, 667, 699).—Azo-compounds containing a carboxylic group in the *ortho*-position do not react normally with phosphorus pentachloride, but yield a 3-hydroxyindazyl derivative chlorinated in the ring; thus benzene-*o*-azobenzoic acid yields *chloro-3-hydroxy-2-phenylindazole*,



which crystallises in white plates, melts at 265°, is soluble in acetic acid, and almost insoluble in benzene or chloroform, and yields *benzene-o-azochlorobenzoic acid*, $CO_2H\cdot C_6H_3Cl\cdot N_2\cdot Ph$, on oxidation with chromic acid or dilute nitric acid, which melts at 124—125°.

The *lactone* of *chloro-3-hydroxy-o-indazylbenzoic acid*,



obtained by decomposing with water the product of the action of phosphorus pentachloride on *o*-azobenzoic acid, forms thin needles which melt at 241°, is soluble in benzene, and is converted by nitric acid into chlorodinitrobenzeneazobenzoic acid melting at 225°. M. A. W.

Nitration of 2-Hydroxy-1-diazonaphthalene-4-sulphonic Acid. ANILINFARBEN- & EXTRACT-FABRIKEN VORM. J. R. GEIGY (D.R.-P. 164665).—Well-dried powdered 2-hydroxy-1-diazonaphthalene-4-sulphonic acid dissolved in cold concentrated sulphuric acid was gradually treated at 0—5° with a mixture of concentrated nitric and sulphuric acids; the mixture was stirred for four hours, allowed to attain a temperature of 15°, and then poured on to ice, when *nitro-2-hydroxy-1-diazonaphthalene-4-sulphonic acid* separated in the form of pale yellow crystals, which can be dried at 80—100° and are not explosive. The new nitrodiazo-derivative, which is more soluble than the unnitrated compound, readily condenses with phenols to yield azo-colouring matters. G. T. M.

The Electrical Charge of Proteid and its Significance. WOLFGANG PAULI (*Chem. Centr.*, 1906, i, 376—377; from *Naturw. Rundsch.*, **21**, 3—5, 17—20).—The serum proteids free from electrolytes have no electrical charge; addition of neutral salts leaves them unchanged, so also does alcohol, which precipitates them readily. Traces of acid or alkali confer on them a positive or negative charge respectively, and hinder their precipitability by alcohol. The differently charged proteids behave in a reverse manner to various ions. The naturally occurring proteids are electro-negative, and the electrical properties of cells and tissues are believed to depend on the charge in their proteid constituents. The similarity between the reactions of colloids and immune substances and between the reactions of the latter substances and fertilisation phenomena is pointed out.

W. D. H.

Optical Rotation and Density of Alcoholic Solutions of Gliadin. W. E. MATHEWSON (*J. Amer. Chem. Soc.*, 1906, **28**, 624—628).—An investigation has been made of the variation in the specific rotatory power of gliadin with changes of temperature, concentration, and the nature of the solvent. It has been found that the specific rotation of a solution in 70—75 per cent. alcohol is practically independent of the concentration of the gliadin. Solutions of the proteid in 70—80 per cent. alcohol show a marked increase in specific rotation as the percentage of water in the solvent increases. A rise of temperature between 20° and 45° produces a slight increase in the specific rotation.

Fleurent (*Compt. rend.*, 1901, **132**, 1421) has described a method for the estimation of gliadin in flours based on the sp. gr. of the alcoholic extract. It is now shown, however, that the differences in the sp. gr. in such cases are too small to afford accurate results.

E. G.

The Amount of Glycine in Milk Proteids. EMIL ABDERHALDEN and A. HUNTER (*Zeit. physiol. Chem.*, 1906, **47**, 404—406).—Skraup (this vol., i, 123) states that caseinogen contains glycine. This is not the case for the pure substance prepared by Hammarsten's process. The mixed coagulable proteids of milk (lactalbumin and lactoglobulin) yield a small quantity, 1·2 grams of glycine-hydrochloride from 100 grams of the proteid material. Whether this is derived from the albumin or globulin or both is not decided. W. D. H.

The Monoamino-acids of Legumin. Emil Abderhalden and Boris Babkin (*Zeit. physiol. Chem.*, 1906, **47**, 354—358. Compare this vol., i, 56).—Legumin prepared from white beans yields on hydrolysis: glycine, 1; alanine, 2·8; aminovaleric acid, 1; leucine, 8·2; pyrrolidine-2-carboxylic acid, 2·3; phenylalanine, 2; glutamic acid, 16·3; aspartic acid, 4; and tyrosine, 2·8 per cent. The numbers obtained resemble those obtained from conglutin. Conglutin yields 19·5 per cent. of glutamic acid; this corrects a previous statement of the authors, that the yield is low. W. D. H.

Physical Chemistry of Oxyhæmoglobin. The Capacity for Combining with Alkali of the Colouring Matter of Blood. Emil Abel and Otto von Fürth (*Zeit. Elektrochem.*, 1906, **12**, 349—359).—Sodium hydroxide is added to solutions of hæmoglobin, and the concentration of the hydroxyl ions in the resulting solution determined by means of a hydrogen electrode. By comparing the actual concentrations found with those calculated from the quantity of sodium hydroxide added, it is found that 51 mg. of sodium hydroxide are neutralised by one gram of hæmoglobin. The compound is hydrolysed to a considerable extent; if no excess of sodium hydroxide has been added, the hydrolysis amounts to about 18 per cent.

Similar experiments with oxyhæmoglobin were not very successful; the results were not sufficiently definite to admit of any calculation of the concentration of the hydroxyl ions. T. E.

Action of Quinine on Hæmoglobin. Hugo Marx (*Chem. Centr.*, 1906, i, 1443; from *Arch. exp. Path. Pharm.*, **54**, 460—464).—The addition of quinine to blood (fresh or dry) changes the colour to brown, and spectroscopically a well-marked band in the red is seen. Brown crystals separate out; similar results follow the action of quinine on aceto-hæmin crystals. If hæmatoporphyrin hydrochloride is dissolved in a concentrated solution of quinine, the latter substance is precipitated in a crystalline form which carries down the pigment with it. W. D. H.

Neuræmin. Gablin & Cie. (*Chem. Centr.*, 1906, i, 563; from *Pharm. Zeit.*, 1906, **51**, 77).—*Neuræmin* is prepared by slowly adding a solution of 10 grams of hæmatin and 10 grams of smilacin in two litres of 90 per cent. alcohol to a solution of 20 grams of lecithin in 100 grams of ether; on distilling off the solvents in a vacuum at 30°, the neuræmin is obtained in the form of a reddish-brown, wax-like solid, which melts at 128° and is readily soluble in alcohol, ether, or acetone. P. H.

The Cleavage Products of Spongin with Acids. EMIL ABDERHALDEN and EDUARD STRAUSS (*Zeit. physiol. Chem.*, 1906, 48, 49—53).—In many of the so-called albuminoids (using the term in the limited sense usual among physiologists), typical cleavage products are absent; for instance, tyrosine is absent from gelatin and spongin. Phenylalanine is absent from spongin and keratin. Pyrrolidine-2-carboxylic acid, glycine, and glutamic acid (in large quantities) are obtained from spongin. The transformation of ordinary proteids into such skeletal substances appears to be a result of metabolism and of the action of tissue enzymes. W. D. H.

Decomposition of Histidine. SIGMUND FRÄNKEL (*Beitr. chem. Physiol. Path.*, 1906, 8, 156—162. Compare Abstr., 1903, i, 650; Pauly, *ibid.*, 1904, i, 1068; Knoop and Windaus, *ibid.*, 1905, i, 834).—*Chlorohistidinecarboxylic acid*, $C_6H_7O_2N_2Cl$, is formed when histidine hydrochloride is treated with nitrous acid at 0°, and the syrup thus obtained reduced with zinc and acetic acid. It crystallises from water in long, transparent plates containing H_2O and melts at 80°. When reduced, it yields *histidinecarboxylic acid* in the form of small crystals, melting at 195° and readily soluble in water. When oxidised with dichromate and sulphuric acid, histidine yields acetic acid and hydrogen cyanide, and when heated at 220° with 20 per cent. hydrochloric acid it yields racemic histidine hydrochloride melting at 220°. When benzoylated by the Schotten-Baumann method, histidine yields a *monobenzoyl* derivative which melts and decomposes at 230°. Even when a large excess of benzoyl chloride is used, no rupture of the ring occurs, and this is regarded as a strong argument against the iminazole formula suggested by Pauly (compare Bamberger and Berlé, Abstr., 1892, 632). Histidinecarboxylic acid cannot be benzoylated. When the hydrochloride of the base is heated above its melting point, carbon dioxide is evolved and a small amount of a *compound*, $C_4H_6O_2N_2$, can be isolated. Fuming nitric acid reacts with histidine, yielding a yellow, crystalline compound containing water of crystallisation. The anhydrous compound has the composition $C_4H_7O_5N_3$.

Formic acid and a compound, $C_4H_6O_2N_2,2H_2O$, which melts at 247° when anhydrous, are formed when histidine is heated with barium hydroxide and water in an autoclave. The *benzoyl* derivative,

$$C_4H_5O_2N_2\cdot COPh,H_2O,$$

melts at 225°. J. J. S.

Diastatic Saccharification. LÉON MAQUENNE and EUGÈNE ROUX (*Compt. rend.*, 1906, 142, 1059—1065. Compare this vol., i, 327).—Further experiments on the action of amylase on starch mucilage show that the optimum condition (slightly alkaline liquid) for the production of dextrin is also that which ensures the largest yield of maltose. In a neutral liquid, more maltose may be produced at first, but the reaction stops sooner and the amount of maltose ultimately produced is smaller.

Crude starch contains two products, one readily attacked by amylase and the other (amylopectin) more resistant, but it is also eventually converted into maltose by the enzyme. The neutralisation of amylase solutions by acids diminishes the stability of the enzyme. The addition of small quantities of acid to starch mucilage undergoing hydrolysis by amylase accelerates the production of maltose, but the addition of further quantities diminishes the activity. Hence it appears probable that amylase occurs in its solutions in combination with a mineral or amino-base forming a kind of zymogen more stable than amylase itself, and that it is liberated from the zymogen by the addition of small quantities of acid.

Solutions of amylase which have been partially neutralised by acid frequently show a change in reaction as saccharification proceeds and tend to revert to the original alkaline condition. The alkali probably results from the decomposition of proteids in the amylase solution by proteolytic enzymes. T. A. H.

Influence of Chemical Constitution on the Lipolytic Hydrolysis of Esters. Joseph H. Kastle (*Chem. Centr.*, 1906, i, 1536—1537; from *Public Health and Marine-Hospital Service of U.S. Hygienic Lab. Bull.* No. 26, 43—51).—Experiments show that whilst the methyl, ethyl, butyl, *iso*butyl, allyl, and benzyl groups have almost the same effect on the hydrolysis of esters by the action of lipase (from liver), the presence of acyl groups in the homologous series has a considerable influence on the reaction. The quantity of an ester of propionic acid which is attacked in a given time is almost exactly the mean of the quantities of the esters of acetic and butyric acids which are hydrolysed under similar conditions. The action on a formic acid ester is a little more rapid than on an acetic acid ester, but there is practically no difference in the velocity of the action on ethyl butyrate and *iso*butyrate. Experiments with methyl β-iodopropionate, ethyl acetate, and ethyl butyrate show that the introduction of the iodine atom in the β-position does not tend to retard the action of lipase, but rather to accelerate it. The introduction of cyanogen into an ester of acetic acid does not affect the action very considerably, the velocity being reduced at most by half; the retarding influence of the cyanoacetic acid becomes more apparent, however, when the experiment is prolonged. E. W. W.

Action of Radium Rays on Tyrosinase. Edith G. Willcock (*J. Physiol.*, 1906, 34, 207—209).—Tyrosinase is an exception to the general rule that radium emanations injure ferments. It may be that the rays bring about oxidation of ordinary ferments, but that oxydase is not itself readily oxidisable, but this view is not strongly urged.

In some cases, where the ferment seemed to be strengthened by exposure to the rays, the result was at first regarded as due to a small amount of hydrogen peroxide formed in the medium. Fenton has shown that radium rays produce this substance from water; this view was not confirmed on examination, for neither glycerol nor water exposed to the rays strengthened the ferment. W. D. H.

Organic Chemistry.

Volatility in Various Groups of Compounds. Louis Henry (*Bull. Acad. roy. Belg.*, 1906, 187—197. Compare Abstr., 1904, i, 466).—*Nitrogen and Phosphorus Compounds.*—The difference between the boiling points of ammonia and hydrogen phosphide is approximately the same as that between the boiling points of hydrazine and liquid hydrogen phosphide. Similarly, the rise in boiling point due to the substitution of H by NH_2 in ammonia is practically the same as that for the replacement of H by PH_2 in hydrogen phosphide.

The replacement of a hydrogen atom by an alkyl group in hydrogen phosphide leads to a greater diminution of volatility than the analogous substitution in ammonia. The replacement of the last hydrogen atom in ammonia by CH_3 leads to an increase in volatility, dimethylamine boiling at 7° and trimethylamine at 3°. In the case of hydrazine, the substitution of an ethyl group for a hydrogen atom leads to an increase of volatility but the effect is less than that due to the substitution of a hydrogen atom by a methyl group. In this respect, hydrazine resembles water, and the phenomenon in both cases is probably due to the fact that water and hydrazine are associated whilst alkyl derivatives are not. The two amino-groups of hydrazine are equivalent so far as the effect of substitution on volatility is concerned.

Carbon and Silicon Compounds.—It is pointed out that of the analogous hydrides, oxides, sulphides, and alkyl derivatives of these two elements, the silicon compounds are, as is to be expected, the less volatile, although this difference tends to disappear, or even to change its sign, in the case of the corresponding alkyloxy-compounds, thus $C(OEt)_4$ boils at 158—159°, whilst $Si(OEt)_4$ boils at 165°. Among the analogous halogen compounds of the elements, on the other hand, the carbon derivatives are usually the less volatile. This latter fact is not due to difference in degree of association, since several investigators have shown that the two tetrachlorides are associated to about the same extent. T. A. H.

Use of Metallic Oxides as Catalytic Oxidising Agents. Paul Sabatier and Alphonse Mailhe (*Compt. rend.*, 1906, 142, 1394—1395).—A claim for priority (compare Matignon and Trannoy, this vol., ii, 427). The authors have for some time been engaged on the investigation of the catalytic oxidising action of metallic oxides and find that when a mixture of methane and oxygen is passed over heated copper oxide, the latter becomes incandescent and remains so if the heating is discontinued. The hydrocarbon is almost completely burnt to carbon dioxide and water, a small quantity of formaldehyde and formic acid being formed. Similar results are obtained with pentane, hexane, and heptane, and the copper oxide can be replaced by the oxides of cobalt or nickel. M. A. W.

Principle of Partition ("Vertheilungsprincip"). ARTHUR MICHAEL (*Ber.*, 1906, 39, 2138—2143).—A theoretical paper, not suitable for abstraction, further elaborating the author's attempt to account for various organic reactions by considering the sum of the influences exerted by all the atoms in the molecule (Abstr., 1900, i, 321).

A. McK.

Application of the Principle of Partition. III. Action of Chlorine on Hexane. ARTHUR MICHAEL and HAROLD J. TURNER (*Ber.*, 1906, 39, 2153—2156. Compare preceding abstract and this vol., i, 551, 559).—When chlorine is passed into boiling hexane in diffused daylight, the resulting mixture of chlorohexanes contains more than 10 per cent. of α-chlorohexane; more β-chlorohexane than γ-chlorohexane is formed. A. McK.

Preparation of *s*-Tetrachloroethane and Hexachloroethane. FRIEDRICH MICHEL (*Zeit. angew. Chem.*, 1906, 19, 1095—1097).—Disulphur dichloride (S_2Cl_2) mixed with 1 per cent. by weight of reduced iron is saturated with chlorine, the excess of this gas being subsequently removed by a current of carbon dioxide. Dry acetylene is then passed into this liquid, the whole being kept at a temperature of 40°. As soon as the acetylene ceases to be absorbed, the excess is removed by a stream of dry carbon dioxide, and chlorine is once more bubbled through the liquid; the above cycle of changes is then repeated until there appears to be no further absorption. The liquid is finally saturated with acetylene, and is then shaken up with water to remove any chloride of sulphur and distilled with steam. The oily distillate, after washing with sodium carbonate, is fractionally distilled, when a mixture of *s*-tetrachloroethane, pentachloroethane, and hexachloroethane is obtained, the two latter only in small quantity. Hexachloroethane is obtained by alternately passing dry acetylene and dry chlorine into gently boiling disulphur dichloride mixed with from 1 to 2 per cent. of reduced iron and contained in a reflux apparatus. Finally the solution is saturated with chlorine, and, while hot, poured off from a dark, amorphous solid and allowed to cool. A portion of the hexachloroethane hereby crystallises out, and can be purified by sublimation and crystallisation from alcohol; the mother liquors are then put back again and alternately saturated with chlorine and acetylene. P. H.

Decomposition of Copper Sulphate by Methyl Alcohol. VICTOR AUGER (*Compt. rend.*, 1906, 142, 1272—1274. Compare Klepl, Abstr., 1882, 1274; de Bruyn, Abstr., 1893, i, 244; de Forcrand, Abstr., 1886, 524).—Hydrated copper sulphate is soluble to the extent of 11·5 per cent. in methyl alcohol at 0°, and the *basic sulphate*, $3CuSO_4,CuO,4CH_4O$, separates from the solution in the form of rosettes of small, green needles; this compound, which can be obtained in much larger quantity by the prolonged boiling of a 2·5 per cent. solution of copper sulphate in methyl alcohol, or by shaking anhydrous copper sulphate in contact with methyl alcohol for a week, is stable in a vacuum over sulphuric acid, but decomposes slowly at 110° or in contact with moist air.

Pickering has shown (*Chem. News*, 1883, **47**, 181) that when a 1·28 per cent. aqueous solution of copper sulphate is boiled, 2·5 per cent. of the copper is deposited in the form of the basic salt, $6CuO,2SO_3,5H_2O$, but a methyl alcohol solution of the same dilution deposits 73 per cent. of the copper as the above basic salt.

Methyl alcohol decomposes zinc sulphate, forming a basic salt, and also, but to a much less extent, cobalt or nickel sulphates. Ethyl alcohol is much less active than methyl alcohol in promoting the decomposition of copper sulphate. M. A. W.

Application of the Principle of Partition. IV. Addition of Hypochlorous Acid to *iso*Butylene. Arthur Michael and Virgil L. Leighton (*Ber.*, 1906, **39**, 2157—2163. Compare this vol., i, 550, 559). —Markownikoff first showed that the propylene chlorohydrin, formed by the addition of hypochlorous acid to propylene, has the formula

$$OH\cdot CHMe\cdot CH_2Cl$$

and not $CHMeCl\cdot CH_2\cdot OH$. The authors now show that Butleroff and Henry are incorrect in assuming that the chlorohydrin,

$$CMe_2Cl\cdot CH_2\cdot OH,$$

is formed by the addition of hypochlorous acid to *iso*butylene; the isomeric compound, $OH\cdot CMe_2\cdot CH_2Cl$, is produced. The rule is submitted that the addition of hypochlorous acid to α-alkylenes leads to the formation of alkylene chlorohydrins, where the chlorine atom is attached to a terminal carbon atom which was previously unsaturated. This is not actually contradictory to the principle of distribution enunciated by one of the authors.

iso*Butylene chlorohydrin* is a colourless oil which boils at 128° (corr.) and has a sp. gr. 1·0663 at 20°. At the ordinary temperature, it is very slowly decomposed by water into hydrochloric acid and *iso*butaldehyde. Its constitution was deduced from its behaviour on dehydration with phosphoric oxide when chloro*iso*butylene was formed. A. McK.

Application of the Principle of Partition. II. Constitution of the Hexyl Alcohol prepared from Mannitol Hexylene. Arthur Michael and Robert N. Hartman (*Ber.*, 1906, **39**, 2149—2152. Compare this vol., i, 550).—The product obtained by the addition of water to hexylene from mannitol does not consist of β-hexanol alone, but is a mixture of β-hexanol and γ-hexanol. The product was submitted to gentle oxidation and the constitution of the resulting ketone mixture determined by the semicarbazide method (*loc. cit.*). The conclusion is drawn that the hexanol mixture contains about 77 per cent. of β-hexanol and 23 per cent. of γ-hexanol.

A. McK.

Acetyl Chloride as a Reagent for Pinacolyl Alcohols. Maurice Delacre (*Bull. Acad. roy. Belg.*, 1906, 134—139).—Henry's experiments (this vol., i, 329) on the action of acetyl chloride on methyl*tert.*-butylcarbinol and dimethyl*iso*propylcarbinol have been repeated, and in both cases the author obtained, as a principal product, an ester boiling at

135—142°. The dimethyl*iso*propylcarbinol used was prepared by Masson's method (Abstr., 1901, i, 249) and differed slightly in boiling point from that used by Henry.

The author has already shown that in the case of the action of hydrogen bromide on ψ-butylethylene (γγ-dimethyl-Δ^a-butylene) (this vol., i, 476) the course of the reaction is dependent on the purity of the hydrocarbon, and suggests that it will be necessary to repeat Henry's experiments with carefully purified specimens of the two alcohols before his method of differentiating between the *sec.*- and *tert.*-alcohols can be accepted. T. A. H.

Etherates of Magnesium Bromide and Iodide. II. The Monoetherate of Magnesium Bromide. Boris N. Menschutkin (*Zeit. anorg. Chem.*, 1906, **49**, 207—212. Compare Abstr., 1904, i, 215; this vol., i, 131, 132).—The solubility relations of ether and the monoetherate of magnesium bromide have been investigated. The saturated solution of the monoetherate in ether is stable between 30° and 158°, the solubility decreasing regularly from 49·1 to 41 per cent. by weight of magnesium bromide between 0° and 158°; below 30°, addition of a trace of dietherate causes the separation of this substance in crystals, whilst above 158° a second liquid layer is formed with separation of monoetherate. When a quantity of etherate corresponding with about 4 per cent. of magnesium bromide is present, the second layer disappears and the solubility curve can be followed to higher temperatures; at 170°, the solution contains only about 0·13 per cent. of magnesium bromide. The solubility curves of ether in the saturated solution of the monoetherate and of the latter solution in ether have also been determined; the systems are stable between 22·8° and 158°.

The complete results obtained in the present and former papers (Abstr., 1904, i, 215) for the equilibrium relations of ether and the mono- and di-etherates are represented diagrammatically. G. S.

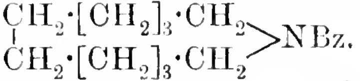
New Synthesis of Methyl Ethyl Xanthate. Harry S. Fry (*J. Amer. Chem. Soc.*, 1906, **28**, 796—798).—When magnesium is allowed to react with a solution of carbon disulphide in methyl alcohol, magnesium methyl xanthate is produced. If the product of the reaction is treated with ethyl bromide and the mixture is afterwards acidified with dilute sulphuric acid, methyl ethyl xanthate, OMe·CS·SEt, is obtained in a yield of 62·5 per cent. of the theoretical. E. G.

Sulphoacetic Acid. Otto Stillich (*J. pr. Chem.*, 1906, [ii], **73**, 538—544. Compare Abstr., 1905, i, 318).—The yield of sulphoacetic acid, obtained on heating glacial acetic acid with sulphuric acid, depends on the temperature and the amount of water present. The product is isolated as barium sulphoacetate, which, when heated with aniline sulphate in aqueous solution, forms *aniline hydrogen sulphoacetate*; this crystallises in glistening, nacreous leaflets and melts at 187—188°. Contrary to Baumstark's statement (*Annalen*, 1866, **140**, 81), the formation of sulphoacetic acid by the interaction of chlorosulphonic and glacial acetic acids commences at 40°, the yield increasing to about 30 per cent. as the temperature rises to 140°; above 80°, carbon dioxide and sulphur dioxide are formed. The barium salt is obtained in an 83 per cent. yield by Franchimont's method (Abstr., 1881, 716) or in a 92 per cent. yield by boiling chloroacetic acid with sodium sulphite and sodium carbonate in aqueous solution and precipitating the product with barium chloride.

Free sulphoacetic acid is prepared by treating the barium salt with sulphuric acid. It is moderately stable towards concentrated sulphuric acid, commencing to evolve carbon dioxide at 190° and sulphur dioxide only at 210° (compare Carius, *Annalen*, 1862, **124**, 55).

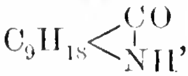
Ammonium sulphoacetate, $C_2H_2O_5S(NH_4)_2$, crystallises in needles, melts at 153—173°, is not hygroscopic, and has an acid reaction to litmus. The *strontium* salt, $C_2H_2O_5SSr,H_2O$, formed by adding strontium chloride to the barium salt in aqueous solution, crystallises in pointed needles and loses H_2O at 230—240°. The calcium salt forms small prisms containing $1\frac{1}{6}H_2O$ (compare Franchimont, Abstr. 1888, 1177). G. Y.

Derivatives of Sebacic Acid. FRIEDRICH KRAFFT (*Ber.*, 1906, **39**, 2193—2197. Compare Phookan and Krafft, Abstr., 1892, 1180).—Decamethyleneimine hydrochloride is obtained in a 65—70 per cent. yield if the mixture of sodium chloride and decamethylenediamine formed by reduction of sebacamide is heated under 100—120 mm. pressure. The free base, boiling at 100—102° under 13 mm. pressure, reacts with benzoyl chloride in a freezing mixture, forming *benzoyldecamethyleneimine*,



$$\begin{matrix}CH_2\cdot[CH_2]_3\cdot CH_2\\ | \\ CH_2\cdot[CH_2]_3\cdot CH_2\end{matrix}\!\!>NBz.$$

This melts at 27·5—28°, boils at 175° in a vacuum, is readily soluble in alcohol or ether, and when oxidised by aqueous potassium permanganate at 35—40° yields *benzoyl*-i-*aminodecoic acid*, $NHBz\cdot[CH_2]_9\cdot CO_2H$, which separates from alcohol or hot water in small, white crystals and melts at 74°. The *barium* salt, $(C_{17}H_{24}O_3N)_2Ba$, is described. When heated in a vacuum, the acid decomposes, forming i-*aminodecoic anhydride*,



$$C_9H_{18}\!<\!\begin{matrix}CO\\ | \\ NH\end{matrix},$$

which solidifies to a white, crystalline mass, melts at 64—66°, and boils at 200—205° in a vacuum.

The *hydrochloride* of *i*-aminodecoic acid is formed by heating the benzoyl derivative with concentrated hydrochloric acid at 110—120° in a sealed tube; it forms deliquescent crystals, and when treated with silver oxide yields the free *acid*, $NH_2\cdot[CH_2]_9\cdot CO_2H$. This melts and decomposes at 164°, is readily soluble in water, but less so in alcohol, and is insoluble in ether. The *platinichloride*, $(C_{10}H_{21}O_2N)_2,H_2PtCl_6$, was analysed. G. Y.

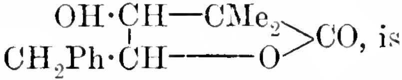
Abnormal Dehydration of Hydroxyalkylpivalic Esters. I. EDMOND E. BLAISE and ALFRED P. COURTOT (*Bull. Soc. chim.*, 1906, [iii], **35**, 360—373. Compare following abstract).—*Ethyl β-hydroxy-β-vinylpivalate* [*β-hydroxy-αα-dimethyl-Δγ-pentenoate*],

$$CH_2:CH\cdot CH(OH)\cdot CMe_2\cdot CO_2Et,$$

prepared by condensing ethyl bromo*iso*butyrate with acraldehyde, is a viscous liquid and boils at 106° under 19 mm. pressure. The *phenylurethane* of the ester is crystalline and melts at 66°. The *free acid* obtained by hydrolysing the ethyl ester with alcoholic potash is viscous, boils at 159° under 23 mm. pressure, and on bromination yields an amorphous *dibromide*. The *calcium* and *barium* salts crystallise with 3 and 5 mols. of water respectively. The *phenylurethane* of the acid crystallises in needles from a mixture of benzene and light petroleum and melts at 90—95°.

When ethyl β-hydroxy-αα-dimethyl-Δ^γ^-pentenoate is dehydrated with phosphoric oxide in presence of benzene, a mixture of gaseous and liquid hydrocarbons, tetramethylsuccinic acid, and some δ-phenyl-αα-dimethyl-Δ^{β}-pentenoic acid are produced. When the operation is conducted in presence of toluene, a mixture of *o*- and *p*-tolyldimethyl-Δ^{β}-pentenoic acids is formed, whilst in presence of chloroform much gas is evolved and almost complete decomposition ensues. *γ-Benzyl-αα-dimethylvinylacetic acid* [*δ-phenyl-αα-dimethyl-Δ^{β}-pentenoic acid*],

$$CH_2Ph\cdot CH\!:\!CH\cdot CMe_2\cdot CO_2H,$$

best purified through its *calcium* salt, is a viscous liquid and boils at 195° under 20 mm. pressure, and on bromination yields an oily unstable *dibromide*. The *methyl* ester, best obtained by the interaction of the acid chloride with methyl alcohol, is liquid and boils at 154° under 17 mm. pressure. The *ethyl* ester, similarly prepared, boils at 154° under 12 mm. pressure. The *acid chloride* is a liquid with a disagreeable, irritating odour, and boils at 158—159° under 20 mm. pressure. The *amide* crystallises from ether in silky spangles and melts at 104—105°; the *anilide* separates from a mixture of ether and light petroleum in long prisms and melts at 90°, and the *phenylhydrazide* is crystalline and melts at 99°. *β-Hydroxy-δ-phenyl-αα-dimethyl-γ-valerolactone*,  $\begin{array}{l}OH\cdot CH—CMe_2\\ CH_2Ph\cdot CH——O\end{array}\!\!>CO$, is obtained by careful oxidation of δ-phenyl-αα-dimethyl-Δ^{β}-pentenoic acid with potassium permanganate. It crystallises from a mixture of benzene and light petroleum and melts at 100°. The final oxidation products of δ-phenyl-αα-dimethyl-Δ^{β}-pentenoic acid are dimethylmalonic and benzoic acids, the latter being probably formed from phenylacetic acid.

The *δ-tolyl-αα-dimethyl-Δ^{β}-pentenoic acid*, obtained on dehydrating ethyl hydroxydimethylpentenoate in presence of toluene, is a viscous liquid and boils at 199° under 16 mm. pressure, and must consist of a mixture of the ortho- and para-derivatives, since on oxidation with permanganate it yields a mixture of terephthalic and *p*- and *o*-toluic acids. The other oxidation products are *o*- and *p*-tolualdehyde, identified by their *semicarbazones*, which melt respectively at 212° and 234°, and dimethylmalonic acid. It is pointed out that *p*-toluic acid is not, as is generally stated, readily soluble in warm water or steam.

T. A. H.

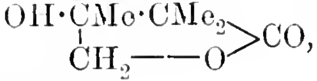
Dehydration of β-Hydroxy-β-alkylpivalic Esters. Parts III and IV. ALFRED P. COURTOT (*Bull. Soc. chim.*, 1906, [iii], **35**, 298—305, 355—360. Compare this vol., i, 230, 396).—Ethyl β-hydroxy-ββ-dimethylpivalate [β-hydroxy-ααβ-trimethylbutyrate],

$OH\cdot CMe_2\cdot CMe_2\cdot CO_2Et$, prepared by condensing acetone with ethyl bromo*iso*butyrate, boils at 91° under 17 mm. pressure (compare Reformatsky and Plesconossoff, Abstr., 1896, i, 128). The *acetyl* derivative is a viscous liquid and boils at 119° under 23 mm. pressure. When dehydrated with phosphoric oxide in the usual way (*loc. cit.*), the ester yields *ethyl αα-dimethyl*iso*propenylacetate* [*ααβ-trimethyl-Δ^β-butenoate*], $CH_2{:}CMe\cdot CMe_2\cdot CO_2Et$. This is a mobile liquid of pleasant odour and boils at 161°. The *methyl* ester is similar and boils at 148°. The *free acid*, obtained with difficulty by hydrolysing the ethyl ester with alcoholic potash, is crystalline, melts at 35°, boils at 117° under 28 mm. pressure, and is very hygroscopic. The hydrated *calcium*, *barium*, and *lead* salts are crystalline. The *chloride* is a mobile liquid with a sharp disagreeable odour and boils at 60° under 30 mm. pressure. The *amide* crystallises from ether in pearly lamellæ and melts at 107—108°, the *anilide* forms needles from a mixture of ether and light petroleum and melts at 61°; the *phenylhydrazide* crystallises from boiling alcohol and melts at 141°; and the *β-naphthylamide* separates from boiling alcohol in small needles and melts at 94°.

βγ-Dibromo-ααβ-trimethylbutyric acid, $CH_2Br\cdot CMeBr\cdot CMe_2\cdot CO_2H$, prepared by brominating *ααβ*-trimethylbutenoic acid in carbon disulphide at 0°, crystallises from a mixture of ether and light petroleum and melts at 125—126°. The *methyl* ester is liquid and boils at 130° under 10 mm. pressure.

On reduction with sodium, ethyl trimethylbutenoate yields the corresponding *ββγ-trimethyl-Δ^γ-butenol*, $CH_2{:}CMe\cdot CMe_2\cdot CH_2\cdot OH$. This is a mobile liquid of slight odour and boils at 152°. The *acetate* has a pleasant odour and boils at 170—171°, and the *phenylurethane* forms splendid needles from light petroleum and melts at 73°.

When oxidised with permanganate, trimethylbutenoic acid furnishes methyl *iso*propyl ketone, trimethylmalic acid, which melts and decomposes at 200—210° (compare Auwers and Campenhausen, Abstr., 1896, i, 424, and Komppa, *ibid.*, i, 597), and *β-hydroxy-ααβ-trimethylbutyrolactone*,



$$\begin{matrix} OH\cdot CMe\cdot CMe_2 \\ | \\ CH_2 \text{——} O \end{matrix} \!\!> CO$$

which crystallises from dry ether and melts at 103°.

Ethyl β-hydroxy-β-phenyl-β-methylpivalate [*β-hydroxy-β-phenyl-αα-dimethylbutyrate*], prepared by condensing acetophenone with ethyl bromo*iso*butyrate, is a syrupy liquid, boils at 154° under 10 mm. pressure, and on treatment with dilute alcoholic potash yields acetophenone and *iso*butyric acid. Some dypnone is produced as a by-product in the primary condensation: *dypnone semicarbazone* crystallises from benzene and melts at 151°. When ethyl β-hydroxy-β-phenyl-*αα*-dimethylbutyrate is dehydrated with phosphoric oxide it yields *ethyl phenyldimethylvinylacetate* [*β-phenyl-αα-dimethyl-Δ^β-butenoate*], $CH_2{:}CPh\cdot CMe_2\cdot CO_2Et$. This is a liquid and boils at 132° under 10 mm. pressure. The *methyl* ester boils at 133° under 19 mm. pressure. The *free acid* is a syrup and boils at 167° under 8 mm. pressure. The *potassium*, *calcium*, and *lead* salts are crystalline. The *chloride* is a mobile liquid of disagreeable odour and boils at 130° under 13 mm. pressure. The *amide* crystallises from ether and melts at 118°, the *anilide* separates from alcohol in needles and melts at

85°, and the *phenylhydrazide* forms lamellæ from alcohol and melts at 159°.

On bromination in carbon disulphide at 0°, phenyldimethylbutenoic acid yields *βγ-dibromo-β-phenyl-αα-dimethylbutyric acid*,

$CH_2Br\cdot CPhBr\cdot CMe_2\cdot CO_2H$,

which crystallises from benzene and melts and decomposes at 165°.

When phenyldimethylbutenoyl chloride is treated with zinc methyl, β-phenyl-αα-dimethyl-β-allyl methyl ketone, $CH_2:CPh\cdot CMe_2\cdot COMe$, is produced. It is a pleasant-smelling liquid, which boils at 123° under 10 mm. pressure. The *semicarbazone* crystallises from alcohol and melts at 192°.

γ-Phenyl-ββ-dimethyl-Δ^{γ}-butenol, $CH_2:CPh\cdot CMe_2\cdot CH_2\cdot OH$, obtained by reducing ethyl phenyldimethylbutenoate with sodium, is a sweet-smelling, syrupy liquid, which boils at 141° under 17 mm. pressure and is not volatile in steam. The *acetate* boils at 145° under 15 mm. pressure. T. A. H.

Xanthophanic and Glaucophanic Acids. CARL LIEBERMANN (*Ber.*, 1906, **39**, 2071—2088).—Claisen's xanthophanic and glaucophanic acids (Abstr., 1897, i, 594) are shown by Zeisel's method to contain respectively two and approximately three ethoxyl groups, and should therefore, the author considers, be called ethyl xanthophanic and ethylglaucophanic acids [xanthophanic acid ethyl ether and glaucophanic acid ethyl ether]. From the chloroform or benzene mother liquor of the crude xanthophanic acid ethyl ether (*loc. cit.*), a *substance*, $C_{26}H_{22}O_5$, is obtained, which crystallises rapidly from alcohol or light petroleum in colourless, glassy needles, contains two ethoxyl groups, melts at 97°, and is very similar to Claisen's ethyl methenylbisacetoacetate, but differs from it by its insolubility in alkalis; the *bromophenylhydrazone*, $C_{26}H_{27}O_4N_2Br$, crystallises in yellow needles and melts at 178°. After the estimation of ethoxyl in this by-product, the de-alkylated residue is obtained from alcohol in colourless needles which melt at 265° and, after sublimation, at 280°; it has an acid reaction and does not give a coloration with ferric chloride.

Xanthophanic acid and glaucophanic acid methyl ethers are obtained in better yield than the corresponding ethyl compounds when methyl methoxymethyleneacetoacetate (2 mols.) and methylsodioacetoacetate (1 mol.) are melted together on the water-bath. The *xanthophanic acid methyl ether*, $C_{16}H_{16}O_8$, is separated from the accompanying sodium glaucophanate methyl ether by solution in chloroform. It separates from benzene in red needles and melts at 179°; from the mother liquor, dark blue metallic prisms are obtained, having the same composition and melting point. *Sodium glaucophanate methyl ether*, $C_{24}H_{19}O_{12}Na$, forms greenish-blue crystals insoluble in chloroform. The *acid*, $C_{24}H_{20}O_{12}$, melts and decomposes at 206°. The by-product in the reaction is a *substance*, $C_{18}H_{18}O_5$, which separates from light petroleum in colourless needles, melts at 133°, is insoluble in alkalis, and contains methoxyl; the de-methylated residue is a colourless acid, melts at 260°, and sublimes in colourless needles.

Sodium methoxide and xanthophanic acid ethyl ether react in benzene solution to form a *substance* which separates from benzene in colourless crystals, melts at 143°, dissolves in alkalis, and gives a red coloration with ferric chloride. Xanthophanic acid methyl ether and glaucophanic acid ethyl and methyl ethers form analogous compounds.

Magnesium methoxide reacts with xanthophanic acid ethyl ether to form a *substance* which crystallises in yellow needles and melts at 160—161°. With glaucophanic acid ethyl ether, magnesium methoxide reacts to form two substances: the one is sparingly soluble in benzene and acetic acid and melts at 213°, the other dissolves readily and melts at 199°; both crystallise in yellow needles and are soluble in a cold solution of sodium carbonate.

Magnesium methoxide and xanthophanic acid methyl ether form a *substance* which crystallises in yellow needles, melts and decomposes at 162°, and forms a *bromophenylhydrazone* melting at 224°. The substance obtained by the action of magnesium methoxide on xanthophanic acid methyl or ethyl ether or on glaucophanic acid ethyl ether is decomposed by a concentrated solution of potassium hydroxide, forming an *acid* which crystallises in white needles, melts and decomposes at 255°, gives a red coloration with ferric chloride, and yields resacetophenone on sublimation; the same acid can be directly obtained from xanthophanic acid ethyl or methyl ether.

Xanthophanic acid ethyl ether reacts with semicarbazide hydrochloride in the presence of methyl alcohol and sodium acetate to form *hydrazodicarbonamide*, $(NH_2{\cdot}CO{\cdot}NH)_2$, which crystallises in colourless needles and melts at 253°, and a *substance*, $C_{19}H_{23}O_8N_3$, which melts at 194°, does not regenerate xanthophanic acid by treatment with hydrochloric acid, and does not show the following characteristic test for the acid. When xanthophanic acid methyl or ethyl ether is warmed with concentrated sulphuric acid, the red colour of the solution suddenly disappears and a yellow, fluorescent solution is obtained, from which can be isolated a *substance*, $C_{14}H_{10}O_7$, which crystallises in golden scales, melts and decomposes at 185°, dissolves in alkali without fluorescence, and forms a brominated derivative melting and decomposing at 270—275°.

When sodium glaucophanate ethyl or methyl ether is warmed with dilute nitric acid, a *substance* is obtained which does not contain nitrogen, crystallises in yellow needles, becomes brown at 170°, melts at 194°, and contains ethoxyl. C. S.

Decomposition of the Oxalates of the Alkaline Earths by Aqueous Solutions of Alkali Sulphates.

H. CANTONI (*Arch. Sci. phys. nat.*, 1906, [iv], 21, 469—494).—Solutions of alkali sulphates were added to the oxalates of the alkaline earths, and the quantity of the oxalate which passed into solution estimated by permanganate. Complete tables of the results are given. In general, potassium sulphate has a greater effect than the sulphates of sodium or ammonium, and the decomposition of the oxalate is greatest for the barium salt and least for the calcium salt. This is what would be expected from the relative solubilities. Thus, in the case of a 4·25*N* solution of potassium sulphate after nine hours, the decomposition by the oxalate of barium reached 50 per cent., by oxalate of strontium 6·88 per cent., and by calcium oxalate 0 per cent. L. M. J.

Preparation of Adipic Acid. Erik Rosenlew (*Ber.*, 1906, **39**, 2202. Compare Mannich, this vol., i, 432).—The conditions are detailed under which adipic acid is obtained in a 70—75 per cent. yield, by the oxidation of *cyclo*hexanone by means of potassium permanganate in sodium carbonate solution. G. Y.

Antimony Tartrate and its Ethyl Ester. J. Bougault (*J. Pharm. Chim.*, 1906, [vi], **23**, 465—469).—Antimonious oxide is dissolved in an aqueous solution of tartaric acid, and the liquid allowed to evaporate spontaneously to a syrup. On the addition of acetone, a precipitate is formed which rapidly becomes crystalline, and consists of the tartrate, $SbC_4H_3O_6$ (this vol., i, 336), containing 1 mol. of acetone, which it loses at 100°. When the anhydrous tartrate is dissolved in a solution of tartaric acid in alcohol, an *ethyl* ester, $SbC_4H_2O_6Et$, slowly separates in small, slender needles. This is dissociated by water with the partial precipitation of antimonious oxide. When dissolved in a solution of potassium hydrogen carbonate, some antimonious oxide is precipitated, but this redissolves on boiling, forming tartar emetic. An aqueous solution of potassium tartrate dissolves the ester, giving potassium ethyl tartrate and tartar emetic. T. A. H.

Methylene Compounds. Louis Henry (*Bull. Acad. roy. Belg.*, 1906, 206—226).—The first portion of this memoir is devoted to the discussion of De Sonay's work (*ibid.*, 1893, **26**, 629, and 1894, **28**, 102) on the chlorination of methyl ether and methylal in the light of the new results obtained by Descudé (see following abstract), and it is pointed out that De Sonay's dichloromethylal probably had the formula $CCl_2(OMe)_2$ in place of $CH_2(O{\cdot}CH_2Cl)_2$ as he supposed. This correction of De Sonay's work indicates that the chlorination of methylal proceeds normally, the hydrogen atom of the methylene group being replaced before those of the methyl groups.

In the second portion of the memoir, a number of analogies between derivatives of "oxymethylene" and the oxides of the heavy metals are pointed out and illustrated by examples, thus: the compound $(CH_2)_3O_2Cl_2$ is regarded as similar in constitution to the mineral mendipite, Pb_3O_2Cl.

In the third section, it is pointed out that ethylidene compounds (methyl derivatives of methylene) may be regarded as forming a series parallel to that of the methylene compounds.

In connection with the order of replacement of hydrogen atoms by chlorine in substances of these types, it is noted that the action of hydrogen chloride on a mixture of acetaldehyde and alcohol gives rise first to the compound $CHMeCl{\cdot}OEt$, and eventually to $CH_2Cl{\cdot}CHCl{\cdot}OEt$, a reaction which appears to be analogous to the production of $CH_2Cl{\cdot}O{\cdot}CH_2Cl$ from $CH_2Cl{\cdot}OMe$, the chlorine in both cases replacing a hydrogen atom in an unattacked methyl group in preference to entering a group in which substitution has already occurred (compare Litterscheid, Abstr., 1904, i, 364). T. A. H.

Order of Substitution of Hydrogen by Chlorine in Methylal. Marcel Descudé (*Bull. Acad. roy. Belg.*, 1906, 198—205).—In addition to the dichloromethyl oxide (Abstr., 1904, i, 546), produced when trioxymethylene is treated with phosphorus trichloride in the presence of zinc chloride, there is formed some *dichloromethylal*, $CH_2(O\cdot CH_2Cl)_2$. This boils at 65—67° under 15 mm. pressure, and with slight decomposition at 166° under atmospheric pressure. It has sp. gr. 1·352 at 11°/11°, and is decomposed immediately by water, yielding hydrogen chloride and formaldehyde, and by alcohols forming water, hydrogen chloride, and monochloromethyl oxide.

When dichloromethyl oxide is heated with trioxymethylene in a closed tube, some dichloromethylal is formed, but the principal reaction is more complex, a *product* which may have the formula

$$O(CH_2\cdot O\cdot CH_2Cl)_2$$

being formed. This is liquid and boils at 100—102° under 15 mm. pressure.

The author points out that the several chlorine derivatives of methylal described by De Sonay (*Bull. Acad. roy. Belg.*, 1893, 26, 647) probably exist, but the boiling points ascribed to them by this author indicate that the constitutions he assigned to them are probably erroneous. T. A. H.

Depression of the Temperature of Reaction in Syntheses with Organic Chloro-compounds. ALFRED WOHL (*Ber.*, 1906, **39**, 1951—1954. Compare Hesse, this vol., i, 375).—The action of β-chloropropaldehyde diethylacetal on potassium cyanide (Wohl, Schäfer, and Thiele, this vol., i, 105) and on ethyl sodiocyanoacetate, of alcoholic ammonia on chloroacetaldehyde diethylacetal and on *p*-chloro- and *o*-chloro-nitrobenzenes, of ethyl chloride on potassium phenoxide, of benzotrichloride on sodium amyloxide, and of *as*-dichloroacetone on sodium acetate take place at lower temperatures and with increased yields if 1/10—1/5 mol. of potassium iodide is added for each atom of chlorine entering into the reaction. The corresponding organic iodo-compound is formed as an intermediate product, the alkali iodide being regenerated in the second stage of the reaction.

Reactions which take place readily, such as that of sodium methoxide on *p*- and on *o*-chloronitrobenzene, are not affected by addition of an alkali iodide. G. Y.

Application of the Principle of Partition. I. Course of the Addition of Water to β-Hexinene. ARTHUR MICHAEL (*Ber*, 1906, **39**, 2143—2148. Compare this vol., i, 550).—The application of the principle of partition enunciated by the author is discussed in the case of the formation of a hexanone by the action of sulphuric acid on Δ^{β}-hexinene.

γ-Hexanone, prepared by the action of an ethereal solution of zinc ethyl on propionyl chloride, boils at 123—123·5° under 765 mm. pressure.

Attempts to separate β-hexanone from γ-hexanone by means of sodium hydrogen sulphite are described. In a mixture of β-hexanone and γ-hexanone, the amount of each may be estimated, since the former forms a semicarbazone with hydrogen semicarbazide phosphate and the latter does not.

The ketone mixture, formed by the action of sulphuric acid on

Δ^{β}-hexinene, was fractionated, and the ratio of β-hexanone to γ-hexanone in each individual fraction was estimated by means of the semicarbazide method described. A. McK.

Melezitose and Turanose. Georges Tanret (*Compt. rend.*, 1906, **142**, 1424—1426. Compare Berthelot, Abstr., 1877, i, 451; Villiers, *ibid.*; Alechin, Abstr., 1886, 683; 1890, 733; Markownikoff, Abstr., 1885, 943).—Melezitose is hydrolysed by heating with 20 per cent. acetic acid solution, yielding turanose and dextrose; after destroying the dextrose by means of yeast, the turanose can be isolated from an alcoholic extract of the residue in the form of transparent, non-crystalline, rounded grains which contain alcohol, have the composition $C_{12}H_{22}O_{11},\frac{1}{2}C_2H_6O$, melt at 60—65°, and lose their alcohol at 100°, yielding the pure sugar, which has $[\alpha]_D$ +71·8°, does not exhibit mutarotation, and has a reducing power of 60, that of dextrose being taken as 100.

Turanose is not attacked by the ordinary soluble ferments, such as emulsin or diastase, but is readily hydrolysed by mineral acids, yielding an equal molecular mixture of dextrose and lævulose, and not dextrose only as stated by Alechin (Abstr., 1890, 733). M. A. W.

Behaviour of Starch on Hydrolysis with Moderately Concentrated Sulphuric Acid. Bernhard Tollens (*Ber.*, 1906, **39**, 2190—2193).—The product of the hydrolysis of potato starch with 8 per cent. sulphuric acid contains dextrose, at most only traces of mannose, and no galactose. The author concludes that the mannose and galactose obtained on hydrolysis of reindeer mosses (Ulander and Tollens, this vol., ii, 193) were derived from the hemicelluloses of the lichens and not from glucoses. G. Y.

Cellulose Acetates. Hermann Ost (*Zeit. angew. Chem.*, 1906, **19**, 993—1000).—The author is of opinion that all the acetates of cellulose described by previous authors are in reality triacetates of substances derived from the hydrolysis of ordinary cellulose.

P. H.

Copper Alkali Cellulose. Wilhelm Normann (*Chem. Zeit.*, 1906, **30**, 584—585).—When cotton wool is treated with a solution of copper hydroxide in sodium hydroxide, it swells up and is converted into a stable copper alkali cellulose, which on analysis is found to contain cellulose and copper oxide in the ratio $C_{12}H_{20}O_{10}:CuO$. The same substance may also be obtained in the form of clear, glassy threads by allowing a fine stream of copper ammonia cellulose to flow into a solution of an alkali hydroxide. P. H.

New Syntheses of Amines by means of Finely-divided Nickel. Alphonse Mailhe (*Chem. Zeit.*, 1906, **30**, 458—459. Compare Abstr., 1905, i, 401, 501).—Nitriles, when reduced by hydrogen in the presence of finely-divided nickel or copper, yield a mixture of primary, secondary, and tertiary amines and ammonia, the reaction probably taking place as follows: (i) $RCN + 2H_2 = RCH_2 \cdot NH_2$;

(ii) $2RCH_2{\cdot}NH_2 = NH(CH_2R)_2 + NH_3$; and (iii) $3RCH_2{\cdot}NH_2 = N(CH_2R)_3 + 2NH_3$. In the case of benzonitrile, the corresponding amines are only formed with copper, nickel giving toluene. Aldoximes or ketoximes similarly give rise to a mixture of primary, secondary, and tertiary amines, but only a very small amount of the latter; the method is a very convenient one for preparing secondary amines of the type $NH(CR^1R^2)_2$. Acid amides, except formamide, likewise yield primary and secondary amines. When nickel is employed as the catalyst, the temperature must not be allowed to exceed 220°, but with copper the temperature may be anywhere between 200° and 300°. P. H.

Resolution of α-Amino*iso*valeric Acid into its Optically Active Components. Emil Fischer, Koichi Matsubara, and Siegfried Hilpert (*Ber.*, 1906, 39, 2320—2328).—The names "valin" and "valyl" are proposed for α-amino*iso*valeric acid and the group $CHMe_2{\cdot}CH(NH_2){\cdot}CO$ respectively.

Formyl-i-*valin*, $C_6H_{11}O_3N$, obtained from *i*-valin like formyl-leucine (this vol., i, 72), separates from hot water in large, rhombic plates, has an acid taste, is easily soluble in alkalis and ammonia, sinters at 137°, and melts at 140—145° (corr.). After treating the hot methyl alcoholic solution with brucine, the salt of *formyl*-l-*valin* separates from the cold liquid in small needles, while the brucine salt of *formyl* d-*valin* is obtained by evaporating the alcoholic mother liquor. The formyl derivatives, liberated by a slight excess of normal sodium hydroxide, separate from hot water in small prisms, sinter at 150°, and melt at 156° (corr.); formyl-*l*-valin has $[\alpha]_D$ at 20°, −13° in alcoholic and 16·9° in aqueous solution, and formyl-*d*-valin has $[\alpha]_D$ 13·05° at 20° in alcoholic solution.

By hydrolysis with 10 per cent. hydrobromic acid, *d*-valin and *l*-valin are obtained in colourless, microscopic, six-sided leaflets. The former melts in a sealed tube at 315° (corr.), sublimes with partial anhydride formation when strongly heated, has a somewhat sweet and bitter taste, and at 20° in 20 per cent. hydrochloric acid has $[\alpha]_D$ 28·75°, and in water 6·42°. *l*-Valin has a sweeter taste than its isomeride, and in 20 per cent. hydrochloric acid has $[\alpha]_D$ −28·72° at 20°.

d-Valinphenylcarbimide (compare Schulze and Winterstein, Abstr., 1902, i, 595) softens at 140°, melts and partially decomposes at 147° (corr.), and by rapid boiling with 20 per cent. hydrochloric acid yields *d*-phenyl*iso*propylhydantoin, which melts at 131—133° (corr.) (124°, Schulze and Winterstein, *loc. cit.*), and has $[\alpha]_D$ −97·5° at 20° in alcoholic solution.

l-Valinphenylcarbimide has $[\alpha]_D$ −19·02° at 20°.

l-Phenyl*iso*propylhydantoin melts at 131—133° (corr.) and has $[\alpha]_D$ 97·22° at 20° in alcoholic solution. C. S.

Salts of Heavy Metals with Feeble Acids and attempts to prepare Colloidal Metallic Oxides. Heinrich Ley and Fritz Werner (*Ber.*, 1906, 39, 2177—2180. Compare Ley, Abstr., 1905, ii, 524; Paal and Leuze, this vol., ii, 356, 358).—Coppersuccinimide is readily prepared by the addition of sodium hydroxide, drop by drop, to a warm aqueous solution of copper acetate and succinimide. *Cobaltsuccinimide*, $(C_4H_4O_2N)_2Co,6H_2O$, formed in the same way from cobalt acetate, is obtained as a salmon-coloured, crystalline precipitate, dissolves in alcohol forming a violet solution, and is hydrolysed on addition of water. *Nickelsuccinimide*, $(C_4H_4O_2N)_2Ni,8H_2O$, prepared from nickel acetate, forms light blue crystals, melts at 110—111°, and is more stable than the preceding salts towards water, forming a green, very dilute aqueous solution at about 30°; when heated this becomes suddenly blue and opalescent, in which state it is stable in absence of air, the nickel hydroxide is thrown down by addition of salts, and the succinimide can be removed partially by hydrolysis.

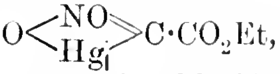
Camphorimide, like succinimide, is a feeble acid. The *copper sodium* salt, $(C_{10}H_{14}O_2N)_2Cu,2C_{10}H_{14}O_2NNa,10H_2O$, is formed by the action of copper acetate on the sodium derivative in concentrated aqueous solution; it forms reddish-violet leaflets and yields blue copper hydroxide when treated with cold water, or a brown hydrated oxide when heated with water. The copper sodium salt is decomposed by acetic acid, camphorimide being formed. G. Y.

Decomposition of Hydroxylamine in Presence of Hydrogen Ferrocyanide: Formation of Crystalline Ferrocyanide-violet and Nitroprusside. KARL A. HOFMANN and H. ARNOLDI (*Ber.*, 1906, **39**, 2204—2208. Compare Hofmann, Abstr., 1905, i, 512; Tanatar, Abstr., 1902, ii, 386).—When boiled with an equal weight of potassium ferrocyanide in aqueous solution, hydroxylamine hydrochloride yields ammonium chloride, potassium nitroprusside, hydrogen cyanide, nitrogen, and *ferric ammonium ferrocyanide*, $Fe'''[(FeC_6N_6)NH_4]_2$, which separates as a deep blue, crystalline powder with purple lustre. It is formed also when hydroxylamine hydrochloride is boiled with potassium ferricyanide in aqueous solution. In its properties, it resembles Williamson's violet. It remains unchanged when treated with water, dilute mineral acids, aqueous oxalic acid, glacial acetic acid, sodium potassium tartrate, or ferric chloride solution, or when boiled with 5 per cent. aqueous potassium hydroxide. The colour remains unchanged when the crystalline violet is digested with hydrogen sulphide solution. Ferric hydroxide is formed only slowly when the salt is digested with 4 per cent. ammonia at the ordinary temperature.

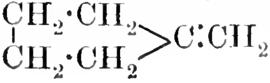
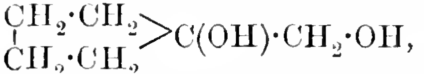
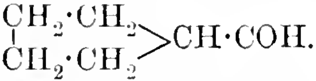
The quantitative examination of the reaction between hydroxylamine and potassium ferrocyanide shows that one-half of the latter forms the nitroprusside, whilst the other is converted into the ferric ammonium ferrocyanide. The hydrogen cyanide formed, which corresponds with one-quarter of the total ferrocyanide, does not enter into reaction with the hydroxylamine, whilst sodium nitroprusside and hydroxylamine hydrochloride form a dull blue powder only on prolonged boiling in aqueous solution. G. Y.

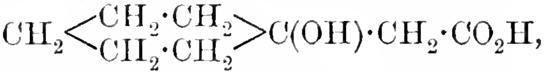
Reduction of Blue Iron-cyanogen Compounds. MORITZ KOHN (*Zeit. anorg. Chem.*, 1906, **49**, 443—444).—Prussian blue and Turnbull's blue can be conveniently and rapidly reduced by the action of a concentrated sodium hydrogen sulphite solution containing a little stannous chloride. The author considers that the reducing action is due to hyposulphurous acid produced by the action of stannous chloride. The statement in the literature, that sulphurous acid is reduced to hydrogen sulphide by stannous chloride, is only true if the latter reagent is present in excess. G. S.

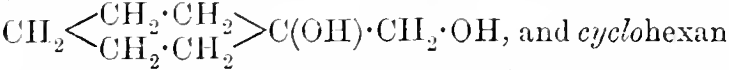
Silicones. Octave Boudouard (*Compt. rend.*, 1906, **142**, 1528—1530).—The grey, amorphous residues, obtained by treating silicon steels containing 0·9 to 5·1 per cent. of silicon with hydrochloric acid until the iron is completely dissolved, have been analysed by Friedel and Ladenburg's method and also by the combustion method. The analytical data indicate that the silicones present in the residues, which evolve hydrogen when treated with alkali hydroxides, are mixtures, in variable proportions, of silicoformic anhydride and silicooxalic acid. The residue obtained from an iron silicide, prepared by the thermite process and containing 10 per cent. of silicon, gave similar analytical numbers. H. M. D.

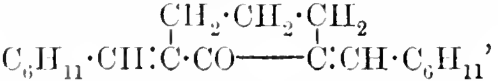
Ethyl Mercuri-*aci*-nitroacetate Anhydride. Roland Scholl and B. Nyberg (*Ber.*, 1906, **39**, 1956—1959. Compare Scholl and Schöfer, Abstr., 1901, i, 359; Hantzsch and Auld, this vol., i, 471).—*Ethyl mercuri*-aci-*nitroacetate anhydride*,  $\mathrm{O}{<}\begin{matrix}\mathrm{NO}\\ \mathrm{Hg}\end{matrix}{>}\mathrm{C\cdot CO_2Et}$, is formed as a white, crystalline precipitate when mercuric chloride is added to a concentrated aqueous solution of ethyl ammonium *aci*-nitroacetate; it sublimes when carefully heated, detonates when strongly heated, and on ignition burns rapidly with a luminous flame. It is almost insoluble in boiling water, but dissolves readily in dilute sodium hydroxide, ammonia, or hydrochloric acid, and is not changed by potassium iodide solution. Mercuric sulphide is precipitated by hydrogen sulphide from the ammoniacal solution, whilst the hydrochloric acid solution yields mercurous chloride when boiled with phosphorous acid. The action of bromine in potassium bromide solution on the aqueous suspension leads to the formation of *ethyl dibromonitroacetate*, $NO_2\cdot CBr_2\cdot CO_2Et$, which is obtained as a colourless liquid boiling at 105° under 11 mm. pressure.

Mercurinitroethyl chloride (Meyer, this Journal, 1874, **27**, 365, 677) has the constitution $NO_2\cdot CHMe\cdot HgCl$, as it dissolves in dilute sodium hydroxide, and when treated with aqueous potassium iodide yields the yellow *iodide*, $NO_2\cdot CHMe\cdot HgI$, which is soluble in an excess of potassium iodide. G. Y.

Terpenes and Ethereal Oils. LXXXI. The Simplest Menthene Hydrocarbons of Various Ring Systems and their Conversion into Alicyclic Aldehydes. Otto Wallach (*Annalen*, 1906, **347**, 316—346. Compare this vol., i, 175, 194, 370).—*cyclo*-Penteneacetic acid (Wallach and Speranski, Abstr., 1902, i, 800) is now found to melt at 51—52°; when slowly distilled it decomposes, forming *methylene*cyclo*pentane*,  $\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}{>}\mathrm{C{:}CH_2}$, which has a penetrating odour of leeks, boils at 78—81°, and has a sp. gr. 0·78 and n_D 1·4355 at 19°. On oxidation with 1 per cent. potassium permanganate solution at 0°, it forms the *glycol*,  $\begin{array}{l}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{array}\!\!>C(OH)\cdot CH_2\cdot OH$, together with pentanone. The *glycol* melts at 39—41°, is readily soluble in all solvents, and when boiled with dilute sulphuric acid loses water, forming cyclo*pentanealdehyde*,  $\begin{array}{l}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{array}\!\!>CH\cdot COH$. This is obtained as an oil which has an odour like valeraldehyde, distils in a current of steam, and forms a *semicarbazone*, $C_7H_{13}ON_3$, crystallising in leaflets and melting at 123—124°. The *nitrosochloride* of methylene*cyclo*pentane, $(C_6H_{10}ONCl)_2$, decomposes at 80—81°, and reacts with piperidine in alcoholic solution, forming the *nitrolamine*, $C_6H_{10}(NO)\cdot C_5H_{10}N$, which crystallises from alcohol and melts at 116—117°. The action of sodium methoxide on the nitrosochloride leads to the formation of a viscid, unsaturated *oxime*, $C_6H_8{:}NOH$, which, on hydrolysis with dilute sulphuric acid, yields *cyclo*pentenealdehyde (v. Baeyer and v. Liebig, Abstr., 1898, i, 638)

[With Eduard Isaac.]—Ethyl *cyclo*hexanolacetate is prepared best by the action of ethyl bromoacetate on *cyclo*hexanone in benzene solution in presence of zinc. The *acid*,  $CH_2\!<\!\begin{array}{l}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{array}\!\!>C(OH)\cdot CH_2\cdot CO_2H$, crystallises from a mixture of benzene and light petroleum and melts at 62—64°.

Methylene*cyclo*hexane (Einhorn and Brandtl, Abstr., 1898, i, 407, 433; Sabatier and Mailhe, Abstr., 1904, i, 666, 809), formed by heating *cyclo*hexeneacetic acid, boils at 105—106°, has a sp. gr. 0·8025 and n_D 1·4501, and closely resembles Δ^1-methyl*cyclo*hexene (Abstr., 1902, i, 750, 806). When oxidised with potassium permanganate, it forms the *glycol*,  $CH_2\!<\!\begin{array}{l}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{array}\!\!>C(OH)\cdot CH_2\cdot OH$, and *cyclo*hexanone. The *glycol* forms large crystals, is stable towards air in the absence of acid vapours, and melts at 76—77°. Hexahydrobenzaldehyde (Bouveault, Abstr., 1904, i, 61; Sabatier and Mailhe, *loc. cit.*) is formed by heating the glycol with dilute acids. It is obtained as an oil which is soluble in water, polymerises readily, boils at 161—163° under the ordinary pressure, and has a sp. gr. 0·9263 and n_D 1·4495 at 19°. The semicarbazone melts at 167—168° (176°; Bouveault, *loc. cit.*). The aldehyde condenses with *cyclo*hexanone in alcoholic sodium hydroxide solution, forming *dihexahydrobenzylidene*cyclo*hexanone*,

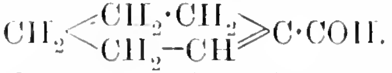


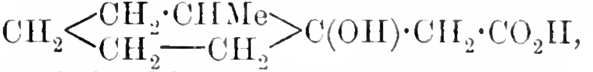
$$\begin{array}{c}CH_2\cdot CH_2\cdot CH_2\\ C_6H_{11}\cdot CH{:}C\cdot CO\text{———}C{:}CH\cdot C_6H_{11}\end{array},$$

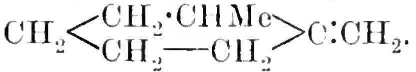
which crystallises in slender needles and melts at 89—90°. With phenylhydrazine, the aldehyde condenses, developing heat and forming a *substance* which crystallises in transparent, red prisms and decomposes on exposure to air. The action of ammonia on the aldehyde in ethereal solution leads to the formation of a *product*, $C_7H_{13}N$, which crystallises in transparent prisms and decomposes at 104—105°.

The *polymeride* of hexahydrobenzaldehyde, $(C_7H_{12}O)_2$, is obtained as a colourless oil, which has only a slight odour, and boils at 150—155°

under 11 mm. pressure. A crystalline *polymeride*, $(C_7H_{12}O)_x$, is formed by the action of sulphuric acid on the aldehyde; it crystallises from ethyl acetate in needles and melts at 195—196° or, after resolidifying, at 202—203°.

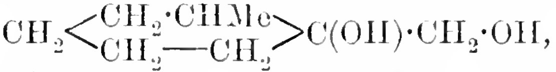
The *nitrosochloride* of methylene*cyclo*hexane, $(C_7H_{12}ONCl)_2$, reacts with piperidine forming the crystalline *nitrolamine*, $C_7H_{12}(NO)\cdot C_5H_{10}N$, which melts at 127°. Elimination of hydrogen chloride from the nitrosochloride leads to the formation of a viscid *oxime*, $C_7H_{10}\!:\!NOH$, which, when hydrolysed with dilute sulphuric acid, yields Δ^1-*tetrahydrobenzaldehyde* (cyclo*hexenealdehyde*),  $CH_2{<}\begin{matrix}CH_2\cdot CH_2\\ CH_2-CH\end{matrix}{>}C\cdot COH$. This is obtained as an oil which has an odour resembling that of benzaldehyde, and forms a *semicarbazone*, $C_8H_{13}ON_3$, melting at 212—213°. Oxidation of the aldehyde by means of silver oxide leads to the formation of Δ^1-tetrahydrobenzoic acid.

[With Erich Beschke.]—2-*Methyl*cyclo*hexane*-1-*ol*-1-*acetic acid*,  $CH_2{<}\begin{matrix}CH_2\cdot CHMe\\ CH_2-CH_2\end{matrix}{>}C(OH)\cdot CH_2\cdot CO_2H$, is formed by condensing 1-methyl*cyclo*hexane-2-one with ethyl bromoacetate in presence of zinc and hydrolysing the resulting ester; it melts at 67—68°. When heated with sodium hydrogen sulphite at 160—170°, the ethyl ester loses water, forming the *ethyl* ester of the unsaturated acid. 1-*Methyl*-Δ^1-cyclo*hexene*-2-*acetic acid* is obtained as an oil, which, when distilled, decomposes and yields 1-*methyl*-2-*methylene*cyclo*hexane*,



$$CH_2{<}\begin{matrix}CH_2\cdot CHMe\\ CH_2-CH_2\end{matrix}{>}C\!:\!CH_2.$$

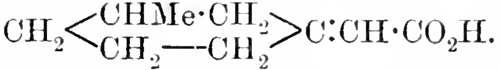
This is obtained in a yield of 84 per cent. of the theoretical, boils at 122—125°, has a sp. gr. 0·808 and n_D 1·4516 at 22°, and is oxidised by permanganate to 1-methyl*cyclo*hexane-2-one and the *glycol*,



$$CH_2{<}\begin{matrix}CH_2\cdot CHMe\\ CH_2-CH_2\end{matrix}{>}C(OH)\cdot CH_2\cdot OH,$$

melting at 59—60°. Hexahydro-*o*-tolualdehyde is obtained only in small quantities when the glycol is heated with dilute acids. The *semicarbazone*, $C_9H_{17}ON_3$, crystallises from boiling water and melts at 136—137°.

The *nitrosochloride* of 1-methyl-2-methylene*cyclo*hexane is solid; the *nitrolamine* formed with piperidine is obtained as a syrup. When heated with dilute sulphuric acid, the *oxime* obtained from the nitrosochloride yields Δ^1-*tetrahydro*-o-*tolualdehyde*, which forms a crystalline *semicarbazone* melting at 208—212°.

The behaviour of 3-methyl*cyclo*hexeneacetic acid (Abstr., 1901, i, 156; Tétry, Abstr., 1902, i, 584) is in accordance with the constitution  $CH_2{<}\begin{matrix}CHMe\cdot CH_2\\ CH_2-CH_2\end{matrix}{>}C\!:\!CH\cdot CO_2H$. The amide is now found to melt at 153—154°; when heated with phosphoric oxide, it forms the *nitrile*, $C_8H_{13}\cdot CN$, which boils at 108—112° under 10 mm., or at 230—234° under the atmospheric pressure, and has an odour resembling that of benzonitrile. With bromine in chloroform solution, the acid forms a crystalline *dibromide*, $C_9H_{14}O_2Br_2$, which melts at 127—129°, and when dissolved in an aqueous alkali carbonate gradually yields an *oil* having the properties of a monobromo-unsaturated compound. 1-*Methyl-3-methylene*cyclo*hexane*, $CH_2<\begin{matrix}CHMe\cdot CH_2\\CH_2—CH_2\end{matrix}>C:CH_2$, formed by slow distillation of 3-methyl*cyclo*hexeneacetic acid, boils at 123—124°, has a sp. gr. 0·794—0·797, n_D 1·4466 at 18° or 1·4461 at 20°, and $[\alpha]_D$ $-29°$ to $-30·22°$, and when oxidised yields 1-methyl*cyclo*hexane-3-one and the *glycol*, $CH_2<\begin{matrix}CHMe\cdot CH_2\\CH_2—CH_2\end{matrix}>C(OH)\cdot CH_2\cdot OH$. This is obtained as a viscid mass, which boils at 150—153° under 39 mm. pressure, and when heated with dilute acids yields hexahydro-*m*-tolualdehyde.

The *nitrosochloride* of 1-methyl-3-methylene*cyclo*hexane, $(C_8H_{14}ONCl)_2$, is obtained in a yield of 15—20 per cent. of the theoretical, and with piperidine forms the *nitrolamine*, $C_8H_{14}(NO)\cdot C_5H_{10}N$, melting at 136—137°. The *oxime* of Δ^1-tetrahydro-*m*-tolualdehyde is formed from the nitrosochloride by the action of alcoholic potassium hydroxide. The *semicarbazone*, $C_9H_{15}ON_3$, melts at 206—207°.

[With EDGAR EVANS.]—4-*Methyl*cyclo*hexane*-1-*ol*-1-*acetic acid*, $CHMe<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>C(OH)\cdot CH_2\cdot CO_2H$, formed by condensing 1-methyl*cyclo*hexane-4-one with methyl bromoacetate and hydrolysing the resulting ester, crystallises from dilute alcohol or boiling water in two forms, of which the one obtained in the greater amount melts at 139·5—140·5°, whilst the other melts at 88—90°. 4-*Methyl*cyclo*hexene*-1-*acetic acid* melts at 42—43° and boils at 137—138° under 14 mm. pressure; the *silver* salt, $C_9H_{13}O_2Ag$, was analysed. 1-*Methyl*-4-*methylene*cyclo*hexane*, $CHMe<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>C:CH_2$, boils at 122—123° and has a sp. gr. 0·7925 and n_D 1·4446 at 22°. The *glycol*, $CHMe<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>C(OH)\cdot CH_2\cdot OH$, crystallises readily, melts at 87—88°, and when heated with dilute acids yields principally a high boiling condensation *product* and a volatile *oil* which does not form a semicarbazone, together with only a small amount of hexahydro-*p*-tolualdehyde. The *semicarbazone* of this melts at 154—156°.

The *nitrosochloride* of 1-methyl-4-methylene*cyclo*hexane is obtained in only a small yield; the *nitrolamine* formed with piperidine melts at 134—135°. Δ^1-*Tetrahydro*-p-*tolualdehyde*, obtained through the *oxime* from the nitrosochloride, forms a *semicarbazone* melting at 192—194°.

G. Y.

Reduction of Partially Hydrogenated Benzenes. AUGUST KLAGES and FRITZ SOMMER (*Ber.*, 1906, **39**, 2306—2315).—The hydrocarbon, $C_{11}H_{16}$, obtained by Rupe and Leichtenhan (this vol., i, 374) is more readily prepared by treating the reaction-product of carvone and magnesium methyl bromide with 40 per cent. sulphuric acid at $-5°$; it is regarded as 2-methyl-$\Delta^{2,6,8(9)}$-menthatriene on account of its conversion into 2-*methyl*-p-*cymene* by a boiling 2 per cent. solution of hydrogen chloride in glacial acetic acid. 2-Methyl-*p*-cymene is a colourless, mobile liquid with the odour of cymene; it boils at 86—87·5° under 16 mm. and at 198° under 732 mm. pressure, is converted into tetrabromo-*o*-xylene by cold bromine and aluminium, and on treatment with fuming sulphuric acid yields two sulphonic acids, the *a-acid*, the chloride of which is solid and forms a *sulphonanilide*, $C_{17}H_{21}O_2NS$, melting at 186—187°, and the *β-acid*, the chloride of which is an oil, and the *anilide*, a crystalline solid which melts at 135—136°.

2-*Methyl*-$\Delta^{6,8(9)}$-*menthadiene-2-ol* (2-*methylcarveol*) is prepared by adding the reaction product of magnesium methyl bromide and carvone, after keeping for one hour, to an ice-cold concentrated solution of ammonium chloride; it is obtained quantitatively as a colourless oil with a faint odour, which boils at 111° under 14 mm. pressure, has a sp. gr. 0·9471 at 20·4°/4°, n_D 1·4911, and $[a]_D$ 36·08° at 20·4°, and is changed by anhydrous oxalic acid at 125° into 2-methyl-*p*-cymene.

2-*Ethyl*-$\Delta^{6,8(9)}$-*menthadiene-2-ol* (2-*ethylcarveol*), prepared in similar manner, is a colourless oil which boils at 118·5—119·5° under 14 mm. pressure, has a sp. gr. 0·9302 at 21°/4°, n_D 1·4879, and $[a]_D$ 31·17° at 21°.

2-*Ethyl*-$\Delta^{2,6,8(9)}$-*menthatriene*, obtained in similar manner to the methyl compound, is a colourless, mobile oil which boils at 100—101° under 13·5 mm. pressure, has a sp. gr. 0·8859 at 18°/4°, n_D 1·5041, and $[a]_D$ 86·19° at 18°, and is converted by 2 per cent. hydrogen chloride in glacial acetic acid into 2-*ethylcymene*, $C_{12}H_{18}$, a colourless oil which boils at 103° under 19 mm. and at 214° under 754 mm. pressure, has a sp. gr. 0·8665 at 21·1°/4°, n_D 1·4965 at 21·1°, is easily soluble in sulphuric acid, and is converted by bromine and aluminium into *pentabromotoluene*, which forms long, colourless needles and melts at 283°.

2-*Phenyl*-$\Delta^{6,8(9)}$-*menthadiene-2-ol* (2-*phenylcarveol*) is a colourless oil which boils at 159—160° under 12 mm. pressure, has a sp. gr. 1·0156 at 15·1°/4°, n_D 1·5562, and $[a]_D$ 81·42° at 15·1°.

2-*Phenyl*-$\Delta^{2,6,8(9)}$-*menthatriene*, containing a little 2-phenyl-*p*-cymene, boils at 152—153° under 13 mm. pressure, has a sp. gr. 0·9882 at 13·8°/4°, n_D 1·5631, and $[a]_D$ 110·2° at 13·8°, and is converted by hydrogen chloride in glacial acetic acid into 2-*phenyl*-p-*cymene*, which can also be obtained from 2-phenylcarveol by anhydrous oxalic acid at 120° or by hydrogen chloride and pyridine at 140°; it is a highly refractive, colourless oil which boils at 268° under 752 mm., or at 153—154° under 14 mm. pressure, has a sp. gr. 0·9822 at 13·8°/4°, n_D 1·5670 at 13·8°, and readily forms a sulphonic acid with fuming sulphuric acid.

C. S.

Action of Magnesium Benzyl Chloride on Mesityl Oxide and Phorone. THEODOR VON FELLENBERG (*Ber.*, 1906, **39**, 2064—2066. Compare Abstr., 1904, i, 961).—*β-Hydroxy-β-benzyl-δ-methyl-*Δ^{γ}-*pentene*, $CMe_2{:}CH{\cdot}C(C_7H_7)Me{\cdot}OH$, prepared from mesityl oxide, is a faintly yellow, somewhat viscous liquid with an agreeable odour; it is slightly volatile in steam, and by distillation under the ordinary pressure yields *β-benzyl-δ-methyl-*$\Delta^{a\gamma}$-*pentadiene*,

$$CMe_2{:}CH{\cdot}C(C_7H_7){:}CH_2,$$

which is a colourless, mobile liquid with an odour of dimethylpentadiene; it boils at 234—236° under 730 mm. pressure.

δ-Hydroxy-δ-benzyl-βζ-dimethyl-$\Delta^{\beta\epsilon}$-*heptadiene*,

$$CMe_2{:}CH{\cdot}C(C_7H_7)(OH){\cdot}CH{:}CMe_2,$$

obtained from phorone, is a viscous, faintly yellow liquid with a pleasant aromatic odour; it is slightly volatile in steam, and by distillation, even under 12 mm. pressure, loses water, forming *δ-benzylidene-βζ-dimethyl-*$\Delta^{\beta\epsilon}$*-heptadiene*, $CMe_2\colon CH\cdot C(\colon CHPh)\cdot CH\colon CMe_2$, which, after repeated distillation, is obtained as a nearly colourless, mobile liquid boiling at 277—278° under 724 mm. pressure. C. S.

Oxidation of Diphenyl Diselenide. M. Stoecker and Friedrich Krafft (*Ber.*, 1906, **39**, 2197—2201. Compare Krafft and Lyons, Abstr., 1896, i, 304).—The nitrate of phenylselenious acid melts and detonates at about 112°; when dissolved in water, neutralised with ammonia, and treated with silver nitrate, it yields *silver phenylselenite*, $SePhO_2Ag$, which is obtained as a crystalline precipitate. The *barium*, $(SePhO_2)_2Ba$, and *copper*, $(SePhO_2)_2Cu$, salts are described. The free *acid*, $SePhO_2H,H_2O$ or $SePh(OH)_3$, prepared by the action of $N/10$ hydrochloric acid on the silver salt, forms a white, crystalline mass, melts at 122—124°, loses H_2O at 100—130° under 15 mm. pressure, and then melts and decomposes at 170°. On reduction with zinc and hydrochloric acid, it forms *phenyl hydrogen selenide*, SeHPh, which boils at 183° and is oxidised by air, forming diphenyl diselenide.

The oxidation of diphenyl diselenide by chlorine in aqueous solution at 50° leads to the formation of *phenylselenic acid*, $SePhO_3H$, which is isolated in the form of its white, crystalline *silver* salt, $SePhO_3Ag$; this detonates feebly when heated. The *barium*, $(SePhO_3)_2Ba$; *copper*, $(SePhO_3)_2Cu$; and *cadmium*, $(SePhO_3)_2Cd$, salts are described. The free *acid* is obtained as a hygroscopic syrup, which is stable when dried at 105°, detonates at 180—190°, forming phenyl diselenide, phenyl selenide, and free selenium, and in moist air forms a *hydrate*, crystallising in glistening prisms. The acid is reduced by concentrated hydrochloric acid, forming phenylselenious acid.

Both these acids deposit red selenium more or less quickly when exposed to light. G. Y.

Alkaloidal Salts of *i-sec*-butylbenzenesulphonic Acid. August Klages (*Ber.*, 1906, **39**, 2131—2135).—Since Klages and Sautter have shown (Abstr., 1904, i, 302) that optically active benzene hydrocarbons can be formed from their sulphonic acids without undergoing racemisation, the author has attempted to resolve *r-sec*-butylbenzenesulphonic acid into its optically active components by the aid of alkaloids. The results were negative.

sec-Butylbenzene, CHMeEtPh, is sulphonated and converted into the barium sulphonate, which, by the action of phosphorus pentachloride, yields *sec-butylbenzenesulphonic chloride* as a colourless oil, which boils at 179—180° under 20 mm. pressure and has a sp. gr. 1·202 at 16·4°/4°; the *anilide* melts at 63—64° and the *sulphonamide* at 80—81°.

Quinine sec-*butylbenzenesulphonate*, $C_4H_9\cdot C_6H_4\cdot SO_3H,C_{20}H_{24}O_2N_2$, prepared by the addition of quinine sulphate to barium *sec*-butylbenzenesulphonate, is sparingly soluble in water, from which it separates in needles. When dried at 110°, it melts at 184° and has $[\alpha]_D$ $-10{\cdot}5^\circ$ at 20° in methyl-alcoholic solution ($c = 1{\cdot}238$). It was not found possible to separate it into two isomeric quinine salts.

Cinchonidine sec-*butylbenzenesulphonate*,

$$C_4H_9{\cdot}C_6H_4{\cdot}SO_3H,C_{19}H_{22}ON_2,$$

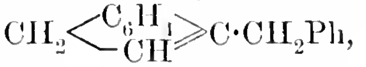
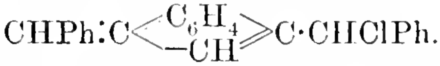
forms glistening needles and, when dried at 110°, melts at 205°. It has $[\alpha]_D$ $-7{\cdot}34^\circ$ at 20° in methyl-alcoholic solution ($c = 1$). The brucine salt is oily.

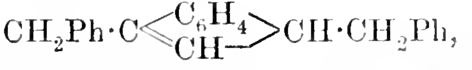
Strychnine sec-*butylbenzenesulphonate*, $C_4H_9{\cdot}C_6H_4{\cdot}SO_3H,C_{21}H_{22}O_2N_2$, separates from benzene in needles, melts at 189—190°, and in methyl-alcoholic solution ($c = 0{\cdot}846$) is optically inactive. A. McK.

Derivatives of Fulvene. I. Condensation of Indene with Aldehydes. Johannes Thiele and Adolf Bühner (*Annalen*, 1906, **347**, 249—274. Compare Thiele, Abstr., 1900, i, 298; 1901, i, 76; Kipping and Hall, Trans., 1900, **77**, 471; Marckwald, Abstr., 1900, i, 434).—The ethylene linking lying outside of the ring of fulvene derivatives is readily reduced by aluminium amalgam in moist ethereal solution if a hydrogen atom of the methylene group is substituted by phenyl or carboxyl. The phenyl group may be attached by an intermediate ethylene linking as in cinnamylidenefluorene,

$$\left.\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\right>C{:}CH{\cdot}CH{:}CHPh.$$

Whilst bisdiphenylene-ethylene is reduced to bisdiphenylene-ethane (compare De la Harpe and van Dorp, Abstr., 1876, i, 242), tetraphenylethylene is not reduced by aluminium amalgam.

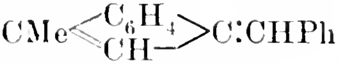
1-*Benzylindene*,  $CH_2{<}\begin{matrix}C_6H_4\\ CH\end{matrix}{>}C{\cdot}CH_2Ph$, formed by reducing benzylideneindene, is obtained as an almost colourless oil, which boils at 183—185° under 13 mm. pressure, is oxidised slowly by air, becoming yellow, gives a yellow coloration with concentrated sulphuric acid, and forms with bromine a *dibromide*, and with amyl nitrite and hydrochloric acid a solid, unstable *nitrosochloride*. It condenses with benzaldehyde in presence of methyl-alcoholic potassium hydroxide, forming 1-*benzyl*-3-*benzylideneindene*,  $CHPh{:}C{<}\begin{matrix}C_6H_4\\ CH\end{matrix}{>}C{\cdot}CH_2Ph$ (compare Abstr., 1901, i, 76). This crystallises from alcohol in glistening, yellow leaflets, melts at 137—137·5°, and gives a violet coloration with concentrated sulphuric acid. It is formed also by distillation at 250—260° under 12 mm. pressure of the colourless hydrocarbon obtained previously (Abstr., 1901, i, 76) by reduction of chlorobenzylbenzylideneindene,  $CHPh{:}C{<}\begin{matrix}C_6H_4\\ CH\end{matrix}{>}C{\cdot}CHClPh$. The results of ebullioscopic molecular weight determinations with the colourless hydrocarbon agree with the formula $C_{23}H_{18}$.

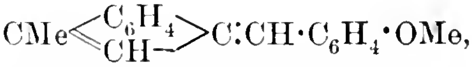
1 : 3-*Dibenzylindene*,  $CH_2Ph{\cdot}C{<}\begin{matrix}C_6H_4\\ CH\end{matrix}{>}CH{\cdot}CH_2Ph$, is formed by reduction of benzylbenzylideneindene; it crystallises from light petroleum in stout, colourless prisms, or from methyl alcohol in white leaflets, melts at 62—63°, when treated with amyl nitrite and hydrochloric acid forms an unstable *nitrosochloride*, and reacts with bromine

in chloroform solution, forming a *dibromide*, $C_{23}H_{20}Br_2$, which separates from light petroleum in stout, colourless crystals and melts and decomposes at 103—104°. When boiled with pyridine, the dibromide loses 2HBr, forming benzylbenzylideneindene.

On preparing Marckwald's viscid benzylindene (*loc. cit.*) and distilling the product in a vacuum, the authors obtained a large fraction which is identical with the product of the reduction of benzylideneindene.

Marckwald's 1-methylindene has been compared and found to be identical with Roser's 3-methylindene (Abstr., 1888, 1303).

3-Benzylidene-1-methylindene,  $\mathrm{CMe}<\genfrac{}{}{0pt}{}{C_6H_4}{CH}>\mathrm{C{:}CHPh}$ (compare Marckwald, *loc. cit.*), is prepared by the condensation of methylindene with benzaldehyde; it crystallises from methyl alcohol, melts at 43—44°, and gives a reddish-violet coloration with concentrated sulphuric acid. On reduction, it yields *3-benzyl-1-methylindene* (?) as a colourless oil, which combines with 1 mol. of bromine, but does not form condensation products.

3-Anisylidene-1-methylindene,  $\mathrm{CMe}<\genfrac{}{}{0pt}{}{C_6H_4}{CH}>\mathrm{C{:}CH{\cdot}C_6H_4{\cdot}OMe}$, formed by the condensation of methylindene with anisaldehyde, crystallises from alcohol in glistening, yellow leaflets, melts at 113°, and gives a violet-blue coloration with concentrated sulphuric acid.

The action of anisaldehyde on indene in presence of methyl-alcoholic potassium hydroxide leads to the formation of anisylideneindene and hydroxyanisylanisylideneindene, which are separated by fractional crystallisation from alcohol.

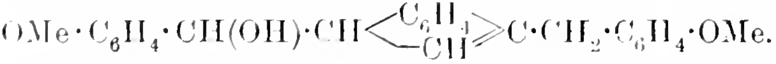
1-Anisylideneindene,  $\mathrm{CH}<\genfrac{}{}{0pt}{}{C_6H_4}{CH}>\mathrm{C{:}CH{\cdot}C_6H_4{\cdot}OMe}$, is obtained as a reddish-yellow, crystalline powder, melts at 118—119°, and gives a greenish-brown coloration with concentrated sulphuric acid. When reduced with aluminium amalgam, it yields *1-anisylindene*,  $\mathrm{CH_2}<\genfrac{}{}{0pt}{}{C_6H_4}{CH}>\mathrm{C{\cdot}CH_2{\cdot}C_6H_4{\cdot}OMe}$, which crystallises in white leaflets, melts at 63—64°, and condenses with anisaldehyde, forming *3-anisyl-1-anisylideneindene*,

$$\mathrm{OMe{\cdot}C_6H_4{\cdot}CH_2{\cdot}C}<\genfrac{}{}{0pt}{}{C_6H_4}{CH}>\mathrm{C{:}CH{\cdot}C_6H_4{\cdot}OMe},$$

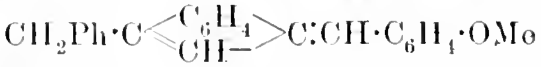
crystallising in yellow leaflets and melting at 111—112°.

a-Hydroxyanisylanisylideneindene,

$$\mathrm{OMe{\cdot}C_6H_4{\cdot}CH(OH){\cdot}C}<\genfrac{}{}{0pt}{}{C_6H_4}{CH}>\mathrm{C{:}CH{\cdot}C_6H_4{\cdot}OMe},$$

crystallises from benzene in small, lemon-yellow leaflets, melts at 141·5—142·5°, gives a bluish-green coloration with concentrated sulphuric acid, and on reduction yields *a-hydroxydianisylindene*,  $\mathrm{OMe{\cdot}C_6H_4{\cdot}CH(OH){\cdot}CH}<\genfrac{}{}{0pt}{}{C_6H_4}{CH}>\mathrm{C{\cdot}CH_2{\cdot}C_6H_4{\cdot}OMe}$. This separates from a mixture of alcohol and ether as a colourless, flocculent substance melting at 175—178°, or from alcohol in a vacuum as a colourless, viscid oil, and when treated with alcoholic potassium hydroxide is converted into anisylanisylideneindene.

Benzylanisylideneindene or *anisylbenzylideneindene*,



$$CH_2Ph\cdot C{<}\genfrac{}{}{0pt}{}{C_6H_4}{CH-}{>}C{:}CH\cdot C_6H_4\cdot OMe$$

or $CHPh{:}C{<}\genfrac{}{}{0pt}{}{C_6H_4}{-CH}{>}C\cdot CH_2\cdot C_6H_4\cdot OMe$, is formed by the action of anisaldehyde on benzylindene or of benzaldehyde on anisylindene; it crystallises from alcohol, melts at 132—133°, and gives an indigo-blue coloration with concentrated sulphuric acid. The identity of the products of the two methods of formation is explained by assuming an oscillation of the ethylene linking (compare Knorr, Abstr., 1894, i, 543; Fischer and Rigaud, Abstr., 1902, i, 188).

p-*Nitro-α-hydroxybenzyl*-p-*nitrobenzylideneindene*,

$$NO_2\cdot C_6H_4\cdot CH(OH)\cdot C{<}\genfrac{}{}{0pt}{}{C_6H_4}{CH-}{>}C{:}CH\cdot C_6H_4\cdot NO_2,$$

prepared by the condensation of indene with *p*-nitrobenzaldehyde in presence of a small quantity of an alkali hydroxide, forms yellow crystals and melts and decomposes at 216—217°.

The reduction of hydroxybenzylbenzylideneindene with aluminium amalgam in moist ethereal solution leads to the formation of the colourless isomeride of benzylbenzylideneindene, together with *hydroxydibenzylindene*, $OH\cdot CHPh\cdot CH{<}\genfrac{}{}{0pt}{}{C_6H_4}{-CH}{>}C\cdot CH_2Ph$, which is obtained as a viscid oil. When distilled in a vacuum, it decomposes, yielding benzaldehyde, benzylbenzylideneindene, and a brown resin, and when treated with alcoholic potassium hydroxide loses water, forming benzylbenzylideneindene.

The residues from the commercial indene used in the above condensations, after complete removal of the indene, yielded an oil which boiled at the same temperature as indene, and on analysis gave figures pointing to the presence of coumarone together with a small amount of hydrindene (compare Weger and Billmann, Abstr., 1903, i, 332).

G. Y.

Derivatives of Fulvene. III. Condensation Products of Fluorene. JOHANNES THIELE and FRANZ HENLE (*Annalen*, 1906, **347**, 290—315. Compare preceding abstract).—The reactivity of the methylene group of fluorene is less than that of indene, which is itself less reactive than *cyclo*pentadiene, that is, the activity decreases as the ethylene linkings of the five-atom ring are rendered inactive by benzene nuclei. The colour of these three substances diminishes in the same order.

Fluorene does not react with aliphatic aldehydes, or with ketones, or with amyl nitrite and sodium ethoxide, but forms condensation products with aromatic aldehydes in presence of alcoholic alkali hydroxides. These products form additive compounds with bromine, and are reduced by aluminium amalgam and moist ether, yielding hydrocarbons of which those having an ethylene linking in the α-position to a phenyl group form additive compounds with picric acid.

Benzylidenefluorene (Abstr., 1900, i, 347) crystallises in rhombic prisms [$a:b:c=0\cdot9912:1:2\cdot6859$], is less soluble than fluorene in organic solvents, and decolorises potassium permanganate in sodium carbonate solution. The *picrate*, $C_{20}H_{14},C_6H_3O_7N_3$, crystallises in orange needles, melts at 115—116°, and is decomposed by water. The *dibromide*, $\begin{array}{l}C_6H_4\\ |\\ C_6H_4\end{array}\!>CBr\cdot CHBrPh$, forms glistening prisms, melts at 112°, and on treatment with zinc dust and glacial acetic acid yields benzylidenefluorene.

Benzylfluorene, $\begin{array}{l}C_6H_4\\ |\\ C_6H_4\end{array}\!>CH\cdot CH_2Ph$, formed by reduction of the benzylidene compound with sodium and amyl alcohol, or in better yield by means of aluminium amalgam, crystallises from light petroleum, melts at 130—131°, and gives with concentrated sulphuric acid a violet coloration, becoming blue and finally disappearing on addition of water.

The action of benzyl chloride and potassium hydroxide on fluorene in a sealed tube at 270°, or on benzylfluorene at 230°, leads to the formation of dibenzylfluorene, which is identical with Weissgerber's supposed benzylfluorene (Abstr., 1901, i, 521). It crystallises in thin prisms and melts at 147—148°.

Anisylidenefluorene, $\begin{array}{l}C_6H_4\\ |\\ C_6H_4\end{array}\!>C:CH\cdot C_6H_4\cdot OMe$, crystallises from glacial acetic acid or ethyl acetate in stout, yellow prisms, melts at 128—129°, is resinified by sulphuric acid and zinc chloride, and on reduction yields *anisylfluorene*, $\begin{array}{l}C_6H_4\\ |\\ C_6H_4\end{array}\!>CH\cdot CH_2\cdot C_6H_4\cdot OMe$. This crystallises from light petroleum in plates and melts at 108—108·5°.

Furfurylidenefluorene, $\begin{array}{l}C_6H_4\\ |\\ C_6H_4\end{array}\!>C:CH\cdot C_4H_3O$, crystallises from alcohol in yellow needles. *Furfurylfluorene*, $\begin{array}{l}C_6H_4\\ |\\ C_6H_4\end{array}\!>CH\cdot CH_2\cdot C_4H_3O$, crystallises in stout, colourless, rhombic prisms and melts at 91—92°.

Bisdiphenylene-ethane, formed by reduction of bisdiphenylene-ethylene with aluminium amalgam, melts at 239—240° (De la Harpe and van Dorp, Abstr., 1876, i, 242).

Cinnamylidenefluorene, $\begin{array}{l}C_6H_4\\ |\\ C_6H_4\end{array}\!>C:CH\cdot CH:CHPh$, is prepared by the action of cinnamaldehyde and sodium ethoxide on fluorene in absolute alcoholic solution at 55°; it crystallises from glacial acetic acid in lemon-yellow needles and melts at 154·5°. The *picrate*,

$$C_{22}H_{16},2C_6H_3O_7N_3,$$

crystallises in needles and melts at 178—179°.

The *picrate* of $a\delta$-diphenyl-$\Delta^{a\gamma}$-butadiene, $C_{16}H_{14},2C_6H_3O_7N_3$ (Thiele and Schleussner, Abstr., 1899, i, 612), crystallises in yellowish-red needles and melts at 152—153°.

Cinnamylidenefluorene dibromide, $\begin{array}{l}C_6H_4\\ |\\ C_6H_4\end{array}\!>C:CH\cdot CHBr\cdot CHBrPh$, formed by the action of bromine on the hydrocarbon in chloroform solution, crystallises in yellow prisms or needles, melts and decomposes at 127°, is decomposed by solvents of high boiling point, and regenerates cinnamylidenefluorene when treated with zinc dust and glacial acetic acid at the ordinary temperature. When oxidised by means of chromic acid in glacial acetic acid solution at 25—30°, it yields dibromodihydrocinnamic acid and fluorenone. The *tetrabromide*,

$\left.\begin{array}{l}C_6H_4\\ |\\ C_6H_4\end{array}\right>CBr\cdot[CHBr]_2\cdot CHBrPh$, is formed by the action of bromine on cinnamylidenefluorene in chloroform solution exposed to bright sunshine; it forms sheaves of crystals, melts and decomposes at about 160°, and yields cinnamylidenefluorene when treated with zinc dust and glacial acetic acid.

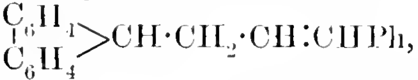
The reduction of cinnamylidenefluorene leads to the formation of bismonohydrocinnamylidenefluorene, which separates from the light petroleum extract of the reduction product, Δ^{β}-dihydrocinnamylidenefluorene, which remains dissolved in the light petroleum, and a hydrocarbon, $(C_{22}H_{17})_x$, which is insoluble in light petroleum.

Δ^{β}-*Dihydrocinnamylidenefluorene*,

$\left.\begin{array}{l}C_6H_4\\ |\\ C_6H_4\end{array}\right>CH\cdot CH\colon CH\cdot CH_2Ph$, separates from alcohol in long, almost colourless, slightly shimmering crystals, melts at 88°, is readily soluble in acetone, ether, benzene, toluene, chloroform, or glacial acetic acid, does not form a picrate, reduces ammoniacal silver nitrate solution at the ordinary temperature, and gives with benzaldehyde and much concentrated sulphuric acid an intense red coloration which is destroyed by addition of water. The *dibromide*, $C_{22}H_{18}Br_2$, crystallises in matted needles, melts at 133°, and forms the Δ^{β}-dihydro-compound when treated with zinc dust and glacial acetic acid, or when heated with methyl-alcoholic potassium hydroxide.

When boiled with sodium ethoxide or piperidine in alcoholic solution, Δ^{β}-dihydrocinnamylidenefluorene is converted into the Δ^{α}-dihydro-isomeride,

$\left.\begin{array}{l}C_6H_4\\ |\\ C_6H_4\end{array}\right>C\colon CH\cdot CH_2\cdot CH_2Ph$ or



$\left.\begin{array}{l}C_6H_4\\ |\\ C_6H_4\end{array}\right>CH\cdot CH_2\cdot CH\colon CHPh$,

which crystallises from alcohol in small, white leaflets, melts at 81—82°, and forms a *picrate*, $C_{22}H_{18},C_6H_3O_7N_3$. This crystallises in glistening, reddish-yellow needles and melts at 128—129°. The *dibromide*, $C_{22}H_{18}Br_2$, crystallises from light petroleum, melts at 94—96°, is decomposed by potassium hydroxide, and forms Δ^{α}-dihydrocinnamylidenefluorene when treated with zinc dust and glacial acetic acid.

Bismonohydrocinnamylidenefluorene, $(C_{22}H_{17})_2$, separates from light petroleum in crystals containing petroleum and melting at about 120°, from acetone in crystals containing acetone and melting at 112—115°, or from glacial acetic acid in glistening crystals, $C_{44}H_{34},C_2H_4O_2$, melting at 124°. The hydrocarbon melts at 160—161° and is readily soluble in hot acetone, benzene, toluene, or chloroform.

The *hydrocarbon*, $(C_{22}H_{17})_x$, crystallises from nitrobenzene, melts at 257° (corr.), and evolves hydrogen bromide when heated with bromine.

G. Y.

New Method for the Preparation of Tetraphenylmethane. Martin Freund (*Ber.*, 1906, **39**, 2237—2238).—Tetraphenylmethane is one of the products resulting from the action of magnesium phenyl bromide on triphenylmethyl bromide; triphenylmethyl peroxide is also formed. A. McK.

Organic Double Salts with Bismuth Chloride. Ludwig Vanino and F. Hartl (*Arch. Pharm.*, 1906, **244**, 216—220).—Compounds of bismuth chloride with the following bases were obtained by mixing the constituents in acetone, alcohol, or ether solution. They are crystalline; and some are, others are not, decomposed by water.

Diphenylamine, $NHPh_2,BiCl_3$. *Nitrosodiphenylamine*, $NO{\cdot}NPh_2,BiCl_3$. *Nitrosodimethylaniline*, $2NO{\cdot}C_6H_4{\cdot}NMe_2,3BiCl_3$. *Aldehyde-ammonia* (really a compound with a polymeric *ethylideneimine*), $(CHMe{\cdot}NH)_3,3BiCl_3$. *Methylamine hydrochloride*, $3NH_3MeCl,2BiCl_3$. *Rheumatine*, $C_{34}H_{34}O_7N_2,2BiCl_3$. *Quinaphenine*, $2C_{27}H_{29}O_3N_3,5BiCl_3$. *Piperazine*, $2C_4H_{10}N_2,3BiCl_3$.

C. F. B.

Formation of Bases from Acetophenone, Formaldehyde, and Ammonium Chloride. H. Schäfer and Bernhard Tollens (*Ber.*, 1906, **39**, 2181—2189. Compare Marle and Tollens, Abstr., 1903, i, 493]; Tollens, Abstr., 1904, i, 507).—The action of formaldehyde and ammonium chloride on acetophenone leads to the formation of *s*-triphenacylomethylamine, *s*-diphenacylomethylamine, and possibly phenacylomethylamine hydrochlorides.

s-Triphenacylomethylamine hydrochloride, $N(CH_2{\cdot}CH_2{\cdot}COPh)_3,HCl$, is extracted from the cold reaction product by means of chloroform; it crystallises in white, microscopic needles, melts at 200—201°, and in dilute alcoholic solution forms precipitates with the alkaloid reagents. The free base, $N(C_9H_9O)_3,\frac{1}{4}H_2O$, crystallises from ether in monoclinic needles. The *sulphate*, $2N(C_9H_9O_3)_3,H_2SO_4$, melts at 180—181°; the *nitrate*, $N(C_9H_9O)_3,HNO_3,\frac{1}{2}H_2O$, forms microscopic needles and melts at 142—143°; the *platinichloride*, $(C_{27}H_{27}O_3N)_2,H_2PtCl_6$, forms a dark yellow, crystalline precipitate and melts at 207°. When boiled with aqueous hydroxylamine in a reflux apparatus, the base evolves ammonia and yields an oil smelling of cinnamaldehyde. In one case, a substance melting at 228° was obtained by boiling the hydrochloride of the base with hydroxylamine hydrochloride in alcoholic solution. With phenylhydrazine, the base forms the phenylhydrazone of phenyl vinyl ketone (Moureu, Abstr., 1894, i, 30), which crystallises in yellow, monoclinic needles, melts at 152—153°, and dissolves in ether, light petroleum, or benzene, forming solutions with deep blue fluorescence. Phenyl vinyl ketone is formed when *s*-triphenacylomethylamine hydrochloride is distilled in a current of steam.

The action of phenylhydrazine on the dibromide of phenyl vinyl ketone leads to the formation of phenylhydrazine hydrobromide.

s-Diphenacylomethylaminehydrochloride, $NH(CH_2{\cdot}CH_2{\cdot}COPh)_2,HCl$, remains in the distillation residue when *s*-triphenacylomethylamine-hydrochloride is heated in a current of steam. It forms a white, crystalline mass, melts when not pure at 136—138°, and forms a *platinichloride*, $(C_{18}H_{19}O_2N)_2,H_2PtCl_6$, melting at about 155°.

G. Y.

Dialkylaminobenzaldehydes. IV. FRANZ SACHS and FRANZ MICHAELIS (*Ber.*, 1906, **39**, 2163—2171. Compare Sachs and Steinert, Abstr., 1904, i, 506; F. and L. Sachs, Abstr., 1905, i, 202).—*Trinitro*-p-*dimethylamino*iso*propylbenzene*, $C_{11}H_{14}N(NO_2)_3$, prepared by nitrating dimethylamino-*p*-*iso*propylbenzene, $NMe_2 \cdot C_6H_4 \cdot CHMe_2$, formed by the action of magnesium methyl iodide on *p*-dimethylaminobenzaldehyde (Sachs and Sachs, *loc. cit.*), separates from dilute alcohol in bluish-yellow needles and melts at 112°.

Trinitro-p-*dimethylamino*iso*amylbenzene*, $NMe_2 \cdot C_6H(NO_2)_3 \cdot CHEt_2$, prepared by nitrating *p*-dimethylamino*iso*amylbenzene,

$$NMe_2 \cdot C_6H_4 \cdot CHEt_2$$

(Sachs and Sachs, *loc. cit.*), separates from alcohol in yellow, hexagonal crystals and melts at 65°.

p-*Dimethylamino*iso*heptylbenzene*, $NMe_2 \cdot C_6H_4 \cdot CHPr_2$, prepared by the action of magnesium propyl bromide on *p*-dimethylaminobenzaldehyde, is a yellow oil and boils at 164° under 24 mm. pressure.

p-*Dimethylaminophenyldi*iso*butylmethane*, $NMe_2 \cdot C_6H_4 \cdot CH(C_4H_9)_2$, prepared from magnesium butyl iodide and *p*-dimethylaminobenzaldehyde, is a yellow oil which boils at 236° under 13 mm. pressure. It gives a reddish-brown coloration with potassium dichromate and sulphuric acids.

p-*Dimethylaminophenyldibenzylmethane*, $NMe_2 \cdot C_6H_4 \cdot CH(CH_2Ph)_2$, prepared from magnesium benzyl chloride and *p*-dimethylaminobenzaldehyde, separates from dilute alcohol in tetragonal prisms and melts at 82°. It gives a dark red coloration with potassium dichromate and sulphuric acid.

p-*Dimethylaminophenyldinaphthylmethane*, $NMe_2 \cdot C_6H_4 \cdot CH(C_{10}H_7)_2$, prepared from magnesium α-naphthyl bromide and *p*-dimethylaminobenzaldehyde, crystallises from carbon disulphide in snow-white needles and melts at 223°.

p-*Diethylamino*iso*propylbenzene*, $NEt_2 \cdot C_6H_4 \cdot CHMe_2$, prepared from magnesium methyl iodide and p-diethylaminobenzaldehyde, is a yellow oil and boils at 156° under 43 mm. pressure.

p-*Diethylamino*iso*heptylbenzene*, $NEt_2 \cdot C_6H_4 \cdot CHPr_2$, prepared from magnesium propyl bromide and *p*-diethylaminobenzaldehyde, is a yellow oil and boils at 165° under 22 mm. pressure.

p-*Diethylaminobenzylidenethiosemicarbazide*,

$$NEt_2 \cdot C_6H_4 \cdot CH{:}N \cdot NH \cdot CS \cdot NH_2,$$

prepared from *p*-diethylaminobenzaldehyde and thiosemicarbazide, forms tetragonal prisms and melts at 180°.

Phenylbenzyl-p-*diethylaminobenzylidenehydrazine*,

$$NEt_2 \cdot C_6H_4 \cdot CH{:}N \cdot NPh \cdot CH_2Ph,$$

prepared from *p*-diethylaminobenzaldehyde and phenylbenzylhydrazine, separates from alcohol in tetragonal prisms and melts at 123°.

p-*Diethylaminobenzylideneacetone*, $NEt_2 \cdot C_6H_4 \cdot CH{:}CH \cdot COMe$, prepared by the addition of acetone and a few drops of alkali to a solution of *p*-ethylaminobenzaldehyde in alcohol, separates in reddish-yellow, spear-shaped crystals and melts at 164°.

p-*Diethylaminobenzylidenemalononitrile*, $\mathrm{NEt_2{\cdot}C_6H_4{\cdot}CH{:}C(CN)_2}$, prepared from *p*-diethylaminobenzaldehyde and malononitrile in presence of a little piperidine, separates from alcohol in yellowish-red, rhombic prisms and melts at 130°.

p-*Diethylaminobenzylidenebenzyl cyanide*, $\mathrm{NEt_2{\cdot}C_6H_4{\cdot}CH{:}CPh{\cdot}CN}$, prepared from *p*-diethylaminobenzaldehyde and benzyl cyanide, crystallises from alcohol in yellow, prismatic needles, and melts at 97°.

p-*Diethylaminobenzylidene*-p-*nitrobenzyl cyanide*,

$$\mathrm{NEt_2{\cdot}C_6H_4{\cdot}CH{:}C(CN){\cdot}C_6H_4{\cdot}NO_2},$$

prepared from *p*-diethylaminobenzaldehyde and *p*-nitrobenzyl cyanide, separates from glacial acetic acid in dark red needles and melts at 206°.

p-*Diethylaminobenzylidenerhodanic acid*,

$$\mathrm{NEt_2{\cdot}C_6H_4{\cdot}CH{:}C}{<}\begin{matrix}\mathrm{CO{\cdot}CS}\\ \quad\ \ |\\ \mathrm{S{-}{-}NH}\end{matrix},$$

prepared from *p*-diethylaminobenzaldehyde and rhodanic acid, separates from alcohol in dark red needles and melts at 182°.

p-*Diethylaminobenzylidenebarbituric acid*,

$$\mathrm{NEt_2{\cdot}C_6H_4{\cdot}CH{:}C}{<}\begin{matrix}\mathrm{CO{\cdot}NH}\\ \mathrm{CO{\cdot}NH}\end{matrix}{>}\mathrm{CO},$$

prepared from *p*-diethylaminobenzaldehyde and barbituric acid, separates from glacial acetic acid in red needles and melts at 129°.

p-*Diethylaminobenzylidenecyanoacetamide*,

$$\mathrm{NEt_2{\cdot}C_6H_4{\cdot}CH{:}C(CN){\cdot}CO{\cdot}NH_2},$$

prepared from *p*-diethylaminobenzaldehyde and cyanoacetamide in the presence of a little piperidine, separates from alcohol in orange, rhombic prisms and melts at 134·5°. A. McK.

Pseudo-acids. ARTHUR HANTZSCH (*Ber.*, 1906, **39**, 2098—2112); HANS EULER (*ibid.*, 2265—2269).—Polemical (compare this vol., i, 415). C. S.

Imide Bromides and their Decomposition. JULIUS VON BRAUN and CARL MÜLLER (*Ber.*, 1906, **39**, 2018—2022. Compare Abstr., 1904, i, 688, 731, 841, 918; 1905, i, 634, 636).—The imide bromides, prepared by the action of phosphorus pentabromide on fatty or aromatic amides, resemble the imide chlorides, but are more readily hydrolysed by moisture. Amides of aliphatic acids react energetically with phosphorus pentabromide, the final products being basic substances which do not form the amide when treated with water.

Benzanilide and phosphorus pentabromide interact, forming the imide bromide, which is obtained as a reddish-yellow, crystalline cake, decomposes when distilled, and with water forms benzanilide. Methylbenzamide, when mixed with phosphorus pentabromide at the ordinary temperature, forms the imide bromide, which, when slightly heated, decomposes into methyl bromide and benzonitrile, a small residue containing cyaphenine remaining on distillation of the products. Similarly, benzylbenzamide yields benzyl bromide and benzonitrile. The imide bromides may be isolated if the reaction with phosphorus pentabromide is carried out in chloroform solution.

The action of phosphorus pentabromide on dibenzoylhexamethylenediamine and on dibenzoylheptamethylenediamine leads to the formation of *αζ*-dibromohexane and *αη*-dibromoheptane, which, on treatment with sodium phenoxide, yield *αζ*-diphenoxyhexane and *αη*-diphenoxyheptane respectively. G. Y.

Action of Nitrous Acid on Tolyl- and *m*-Xylyl-carbamides and on Phenylthiocarbamide. II. J. Haager and R. Doht (*Monatsh.*, 1906, **27**, 267—279. Compare Abstr., 1901, i, 236; Walther and Wlodkowsky, Abstr., 1899, i, 590).—Nitrous acid reacts with *m*- and *p*-tolylcarbamides in the same manner as with phenylcarbamide, forming the nitroso-derivatives in presence of a limited quantity, but the carbamides in presence of an excess, of hydrochloric acid. *o*-Tolyl- and *m*-xylyl-carbamides yield the corresponding carbimides, but not the nitroso-derivatives. Nitrous acid does not react with *α*- and *β*-naphthylcarbamides in hydrochloric acid solution.

m-*Tolylcarbimide*, C_8H_7ON, boils at 183° and behaves towards water, absolute alcohol, and pyridine in the same manner as other carbimides.

Nitroso-*p*-tolylcarbamide melts and decomposes at 85° (83°; Walther and Wlodkowsky, *loc. cit.*).

m-*Xylyl-4-carbimide*, $C_6H_3Me_2\cdot NCO$, formed from *m*-xylyl-4-carbamide by the action of nitrous acid in hydrochloric or of sodium nitrite in glacial acetic acid solution, is obtained as a yellow oil, which boils at 215° and is more stable than other carbimides towards water.

The acid filtrates from the preparation of the nitrosocarbamides and of the carbimides contain the corresponding diazonium chlorides.

Whilst the chief product of the interaction of nitrous acid and phenylthiocarbamide is dianilino-*o*-diazothiole, which melts at 190° (181°; Hector, Abstr., 1889, 872; 1890, 526), a portion of the thiocarbamide reacts with the nitrous acid in the same way as does phenylcarbamide, forming phenylcarbimide. G. Y.

Constitution and Colour of Nitrophenols. Hugo Kauffmann (*Ber.*, 1906, **39**, 1959—1966. Compare Abstr., 1900, i, 480; 1901, i, 318).—The author criticises Hantzsch's views (this vol., i, 353) and concludes that whilst the "quinone theory" of colour explains the colour of nitrophenols, which, according to the "auxochrome theory," should be less highly coloured than the corresponding ethers, the latter theory is of more general applicability.

Contrary to Hantzsch's statement that all nitrophenol ethers incapable of exhibiting tautomerism are colourless, nitroquinol dimethyl ether is yellow. In agreement with the "auxochrome theory" is the colour of sodium *m*-nitrophenoxides and the formation of yellow nitro-derivatives by hydrocarbons, such as chrysene and pyrene.

The methoxy-, acetoxy-, and acetylamino-groups and iodine are only weak, whilst the nitro-, amino-, and dialkylamino-groups are strong auxochromes. The auxochromic influence of bromine is weak and uncertain; that of chlorine is negative. G. Y.

Nitrophenolsulphonic Acids. ROBERT GNEHM and OSKAR KNECHT (*J. pr. Chem.*, 1906, [ii], **73**, 519—537).—Whilst *o*-nitrophenol-*p*-sulphonic acid is formed by the action of fuming sulphuric acid (Kekulé, *Jahresber.*, 1867, 641) or of chlorosulphonic acid on *o*-nitrophenol (Mazurowska, this Journal, 1875, 875; 1876, ii, 61), sulphonation of *o*-nitrophenol in presence of mercury (Iljinski, Abstr., 1904, i, 176; Schmidt, *ibid.*, 256) leads to the formation of a mixture of sulphonic acids, of which *o-nitrophenoltrisulphonic acid* is isolated in the form of its *barium* salt, $C_6HO_{12}NS_3Ba_2$.

o-Nitrophenol-*p*-sulphonic acid crystallises from chloroform in glistening prisms, loses $CHCl_3$ at 80—90°, and melts at 141—142°. The potassium salt crystallises with 1 mol. of water.

m-*Nitrophenolsulphonic acid*, $NO_2\cdot C_6H_3(OH)\cdot SO_3H$, formed from *m*-nitrophenol by the action of fuming sulphuric acid, or in small yields by sulphonation in presence of mercury, crystallises in large, colourless, transparent, hexagonal leaflets containing $4H_2O$ and melting at 50—60°; the anhydrous acid is hygroscopic, melts at 105—107°, when heated above its melting point forms a sublimate of *m*-nitrophenol, and when warmed with bromine water yields dibromo-*m*-nitrophenol (compare Willgerodt and Mohr, Abstr., 1886, 1030). The *sodium*, $C_6H_3O_6NSNa_2$, *sodium hydrogen*, and *barium*,

$$C_6H_3O_6NSBa,H_2O,$$

salts are described.

The *m*-aminophenolsulphonic acid, formed by reduction of the above nitro-acid is probably identical with the acid obtained by direct sulphonation of *m*-aminophenolsulphonic acid (D.R.-P. 83447) and with Klappert's electrolytic reduction product (Abstr., 1903, i, 85). The *barium hydrogen* salt, $(C_6H_6O_4NS)_2Ba,4H_2O$, crystallises in brown needles and prisms. A comparative table of the properties of the known *m*-aminophenols is given.

p-Nitrophenol-*o*-sulphonic acid is obtained in a 45 per cent. yield by direct sulphonation of *p*-nitrophenol (Post, Abstr., 1881, 92). The presence of catalytic agents such as mercury, boric acid, or infusorial earth, or the use of alkali polysulphates, influences the yield, but not the constitution, of the product. *p*-Nitrophenolsulphonic acid cannot be obtained by the action of chlorosulphonic acid on *p*-nitrophenol.

G. Y.

Reaction of an Oxydase Type exhibited by Halogen Derivatives of the Rare Earths. EUGÈNE FOUARD (*Compt. rend.*, 1906, **142**, 1163—1165).—The accelerating action of the chlorides of the metals of the rare earths on the absorption of oxygen by quinol is much greater than the corresponding action of the chlorides of the alkali and alkaline earth metals (this vol., i, 421). The experiments were conducted by placing equal volumes of equivalent solutions of the metallic chlorides together with a definite quantity of a solution of quinol into tubes, which were then sealed and placed in an oil-bath. After eight days the volume of oxygen present in the residual air was measured, and the ratio R between the volume of oxygen absorbed and the original volume of oxygen is given in the following table:

Solution of chloride.	Ratio R per cent.
Samarium chloride	75·75 per cent.
Thorium ,,	63·10 ,,
Cerium ,,	57·71 ,,
Neodymium ,,	54·23 ,,
Praseodymium ,,	53·35 ,,
Lanthanum ,,	22·60 ,,
Sodium ,,	17·82 ,,

M. A. W.

Cholesterol. I. Addition of Hydrogen Chloride. JULIUS MAUTHNER (*Monatsh.*, 1906, **27**, 305—314. Compare Mauthner and Suida, Abstr., 1894, i, 486; 1903, i, 625; 1904, i, 49).—*Chlorocholestanol* (*cholesterol hydrochloride*), $C_{27}H_{45}OCl$, is formed together with β-dichlorocholestane by the action of hydrogen chloride on cholesterol dissolved in a mixture of ether and absolute alcohol cooled by ice; it crystallises from a mixture of chloroform and light petroleum in glistening, pliant, slender needles, melts and decomposes at 154—155°, does not form an additive compound with bromine, and when distilled loses hydrogen chloride, forming cholesterylene. It is decomposed by concentrated sulphuric acid, but is stable towards fuming nitric acid at the ordinary temperature, and when hydrolysed with alcoholic potassium hydroxide or acetate yields cholesterol, together with an oily product, probably an isomeride.

β-Dichlorocholestane, $C_{27}H_{44}Cl_2$, separates slowly from the ethereal-alcoholic filtrate from chlorocholestanol; it crystallises from a mixture of alcohol and benzene in flat needles, melts at 117°, and is stable towards fuming nitric acid, but is decomposed by concentrated sulphuric acid only slowly, forming a solution with slight green fluorescence. The β-dichloro-derivative is formed also by the action of hydrogen chloride on cholesteryl chloride, and is isomeric with cholestene dichloride (α-dichlorocholestane), previously described (Mauthner and Suida, Abstr., 1894, i, 326).

Chlorocholestane, $C_{27}H_{45}Cl$, is formed by the action of hydrogen chloride on cholestene in chloroform solution; it crystallises in glistening, flat prisms or sheaves of iridescent leaflets, commences to sinter at 80°, melts at 91°, dissolves in boiling alcohol, and does not react with bromine in chloroform solution.

The above additive compounds of lævorotatory cholestene, cholesterol, and cholesteryl chloride are dextrorotatory. G. Y.

Cholesterol. VI. ADOLF WINDAUS (*Ber.*, 1906, **39**, 2008—2014. Compare Abstr., 1904, i, 49, 667, 1010; 1905, i, 128; this vol., i, 174; Diels and Abderhalden, this vol., i, 272).—The oxidation of cholestenone by potassium permanganate in neutral solution leads to the formation of (*a*) a small quantity of a *monobasic acid*, $C_{27}H_{44}O_4$, which crystallises from dilute alcohol in long, thin needles and melts at 217—218°, and (*b*) a *keto-acid*, $C_{26}H_{42}O_3$, which crystallises from a mixture of benzene and light petroleum in tetragonal leaflets and melts at 155°. The *oxime*, $C_{26}H_{42}O_2$:N·OH, crystallises in long, thin prisms and melts and decomposes at 191°. When brominated in glacial acetic acid solution, the keto-acid yields the *bromo*-derivative, $C_{26}H_{41}O_3Br$, which crystallises in needles, melts at 154—156°, and forms a *hydroxyketo-acid* when boiled with aqueous potassium hydroxide.

Oxidation of the keto-acid with bromine in aqueous potassium hydroxide leads to the formation of a hygroscopic *tricarboxylic acid*, $C_{26}H_{42}O_6$, which crystallises from benzene in stellate groups of needles, melts at 129—131°, and decomposes when more highly heated.

The author considers that the formation of the keto-acid from cholestenone shows that the latter cannot be an *αβ*-unsaturated ketone. G. Y.

Cholesterol. VII. Adolf Windaus (*Ber.*, 1906, **39**, 2249—2262. Compare Abstr., 1904, i, 49, 667, 1010; 1905, i, 128; this vol., i, 174, and preceding abstract; van Oordt, *Inaug. Diss.*, 1901, Freiburg, i/B).—When a solution of cholesterol in a mixture of benzene and glacial acetic acid is oxidised by chromic acid, one of the products is an acid, $C_{27}H_{44}O_4$, which melts at 290°; its identity with the acid obtained by Diels and Abderhalden (Abstr., 1904, i, 880) as a product of the oxidation of cholesterol with potassium hypobromite was further indicated by its conversion into the monomethyl ester melting at 124°.

When oxycholestenone is heated at 180° for two hours with zinc dust, it is converted into cholestandione, identical with the product which the author had previously obtained from nitrocholesterol. A comparison of the formulæ for oxycholestenone, $C_{27}H_{40}O_2$, and for cholestandione, $C_{27}H_{42}O_2$, shows that in the reduction of the former by zinc dust a hydroxy-group had not been replaced by hydrogen, as would have been the case had oxycholestenone possessed a tertiary hydroxy-group; it is probable, on the other hand, that a simple addition of two hydrogen atoms had been effected. The conversion of oxycholestenone into cholestandione may be carried out quantitatively by reducing it with zinc and acetic acid at a lower temperature than 180°. The conclusion is accordingly drawn that oxycholestenone is an unsaturated diketone.

The presence of an enolic group in oxycholestenone is indicated by the formation of an ethyl ether and a benzyl ether. The ethyl ether is readily hydrolysed.

When oxycholestenone in ethereal solution is acted on by 20 per cent. potassium hydroxide, the yellow potassium salt of oxycholestenone separates and yields the characteristic phenylhydrazone. When this salt is allowed to remain under diminished pressure for several days, it undergoes transformation into a salt of an acid and no longer yields a hydrazone. This observation also supports the view that oxycholestenone contains an enolic group.

The dibromo-derivative of cholestandione is identical with the compound obtained by the addition of bromine to oxycholestenone. By the further action of bromine, each is converted into *tribromocholestandione*, $C_{27}H_{39}O_2Br_3$, which separates from acetone in needles and melts at 195°. The two bromine atoms in oxycholestenone dibromide are probably in the 1 : 2-position.

It is highly probable that the keto-groups in cholestandione and oxycholestenone respectively are in the 1 : 4-position.

The *compound*, $C_{54}H_{85}O_3N$(?), formed by heating cholestandione with alcoholic ammonia for six hours at 120°, separates from a mixture of chloroform and alcohol in needles which melt and decompose at over 300°.

The *compound*, $C_{27}H_{42}N_2$, formed by the action of hydrazine hydrate on cholestandione, separates from a mixture of benzene and methyl alcohol in tetragonal leaflets and softens at about 188°. In the formation of this compound, 1 mol. of the diketone interacts with 1 mol. of hydrazine with the elimination of 2 mols. of water.

The *compound*, $C_{27}H_{42}ON_2$, formed by the action of hydrazine hydrate on oxycholestenone, crystallises in yellow leaflets and melts at 160—161°.

The *compound*, $C_{33}H_{46}ON_2$, formed by the action of *o*-phenylenediamine on oxycholestenone, separates from ethyl acetate in brick-red leaflets and melts at 158—159°.

The *compound*, $C_{27}H_{42}O_6S$(?), formed by the action of acetic anhydride and sulphuric acid on oxycholestenone, separates from benzene in needles and decomposes at about 148°.

The *compound*, $C_{29}H_{45}O_3N$, prepared by the action of hydroxylamine hydrochloride and sodium acetate on β-oxycholestenol acetate, separates from a mixture of benzene and light petroleum in needles and melts at 185—186°.

In cholesterilene, there is no system of conjugated double linkings. It is not acted on by sodium and ethyl (or amyl) alcohol.

Oxycholestenone is formed when cholesterilene is oxidised by chromic acid. A. McK.

Synthesis of Aldehydes and Ketones from *as*-Disubstituted Ethylene Glycols and their Ethers. RICHARD STOERMER, E. (FREIHERR) SCHENCK ZU SCHWEINSBERG, FR. SIBBERN-SIBBERS, and P. RIEBEL (*Ber.*, 1906, **39**, 2288—2306).—*Diphenylphenoxymethylcarbinol*, OH·CPh₂·CH₂·OPh, obtained in 71 per cent. yield by the interaction of magnesium phenyl bromide and ethyl phenoxyacetate, separates from alcohol in large, rhombic crystals and melts at 101°. When heated with alcoholic potash for twenty hours at 200°, it yields two products, diphenylethoxymethylcarbinol (compare Béhal and Sommelet, Abstr., 1904, i, 222), which is identical with the synthetic ether obtained from magnesium phenyl bromide and ethyl ethoxyacetate, and diphenylethyleneglycol (compare Paal and Weidenkaff, this vol., i, 583), the *diacetate* of which melts at 145·5°. Both compounds are changed by boiling 20 per cent. sulphuric acid into diphenylacetaldehyde, the glycol completely, the ether to the extent of two-thirds. Dry diphenylethylene glycol is decomposed by heating, yielding formaldehyde and benzhydrol, the latter being further changed into diphenylmethane and benzophenone.

Benzoylcarbinol is conveniently obtained in good yield by digesting a cold alcoholic solution of bromoacetophenone with excess of potassium acetate; after a short heating on the water-bath, the hot liquid is poured into ice-cold water and the acetate thus obtained purified according to Fischer and Busch's directions (Abstr., 1891, 1514). Benzoylcarbinol reacts with magnesium phenyl bromide to form diphenylethylene glycol, according to the equation

$$COPh\cdot CH_2\cdot OH + 2PhMgBr = OMgBr\cdot CPh_2\cdot CH_2\cdot OMgBr + C_6H_6.$$

In a similar way, diphenylphenoxymethylcarbinol is obtained from phenoxyacetophenone and magnesium phenyl bromide.

Phenoxydi-p-*tolylethylene*, $C(C_7H_7)_2\colon CH\cdot OPh$, is obtained when magnesium *p*-tolyl bromide (2 mols.) reacts with ethyl phenoxyacetate (1 mol.). It crystallises in colourless needles and melts at 122°. When heated for twelve hours at 240° with alcoholic potash, it yields di-*p*-tolylethylene and ethoxydi-*p*-tolylethylene; the latter is converted by hot 20 per cent. hydrochloric acid into *di*-p-*tolylacetaldehyde*, $CH(C_7H_7)_2\cdot CHO$, a colourless oil, which boils at 213° under 26 mm. pressure, reduces Fehling's and silver solutions, and forms an *oxime* crystallising in small, colourless needles and melting at 126·5°, and a *semicarbazone* which melts at 185°.

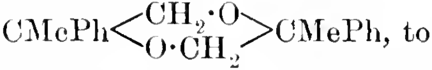
Magnesium *o*-tolyl bromide and ethyl phenoxyacetate react in the normal way, forming *di-o-tolylphenoxymethylcarbinol*,

$$OH\cdot C(C_7H_7)_2\cdot CH_2\cdot OPh,$$

which crystallises in colourless needles and melts at 130°.

Dimethylphenoxymethylcarbinol, $OH\cdot CMe_2\cdot CH_2\cdot OPh$, obtained like the corresponding diphenyl compound, is a colourless oil with a sweet odour, which boils at 119° under 16 mm. and at 231° under the ordinary pressure, and forms a *phenylurethane* which melts at 70°. When heated with alcoholic potash at 200°, it yields dimethylethoxymethylcarbinol (compare Béhal and Sommelet, *loc. cit.*), which is converted by 20 per cent. sulphuric acid into *iso*butaldehyde.

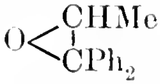
Phenoxymethyldiethylcarbinol, $OPh\cdot CH_2\cdot CEt_2\cdot OH$, boils at 259—260° and forms a *phenylurethane* which melts at 98°. Ethoxymethyldiethylcarbinol yields diethylacetaldehyde by boiling with 20 per cent. sulphuric acid.

β-Phenylpropylene αβ-glycol, $OH\cdot CMePh\cdot CH_2\cdot OH$, to the extent of 7·5, and its *anhydride*,  $CMePh<\substack{CH_2\cdot O \\ O\cdot CH_2}>CMePh$, to the extent of 25 per cent., are obtained by the interaction of magnesium methyl iodide and benzoylcarbinol; they are separated by water, in which the former is easily soluble. The glycol forms colourless needles, melts at 44·5°, boils at 158—160° under 25 mm. pressure, and is partially changed into hydratropaldehyde by 20 per cent. sulphuric acid. The anhydride, which is a yellow, odourless oil boiling at 194° under 15 mm. pressure, is not identical with Klages' oxide (Abstr., 1905, i, 523); it is converted by slightly acidified water at 180° into hydratropaldehyde.

β-Phenylbutylene αβ-glycol, $OH\cdot CEtPh\cdot CH_2\cdot OH$, and its *anhydride*, $C_{20}H_{24}O_2$, are obtained from an ethereal solution of magnesium ethyl iodide and benzoylcarbinol suspended in dry benzene, the relative yields depending on the order in which the one solution is added to the other. The former compound crystallises in needles, melts at 56°, and boils at 158—161° under 20 mm. pressure; the latter is a viscous, yellow oil, which boils at 221—223° under 20 mm. pressure, and is difficultly volatile in steam.

a-Phenylbutaldehyde, CHEtPh·CHO, obtained from the preceding reaction products by slightly acidified water at 180°, is a colourless oil with a strong agreeable odour, which boils at 104—106° under 15 mm. and at 211° under the ordinary pressure; the *oxime* is an oil, but the *semicarbazone*, best obtained from the sodium hydrogen sulphite compound, melts at 155°.

By the action of magnesium phenyl bromide on ethyl *a*-phenoxypropionate, the *phenyl ether* of *ββ*-diphenylpropylene-*aβ*-glycol, $OH\cdot CPh_2\cdot CHMe\cdot OPh$, is obtained, which melts at 136°. Alcoholic potash at 220° converts it into an oil, from which *ββ-diphenylpropylene oxide*,



$$O<\begin{matrix}CHMe\\ |\\ CPh_2\end{matrix}$$

, was isolated, but not the corresponding ethyl ether in the pure state; the former melts at 67°, boils above 300° with slight decomposition, and forms an oily *chlorohydrin*, $C_{15}H_{15}OCl$.

aa-Diphenylpropylene aβ-glycol, $OH\cdot CPh_2\cdot CHMe\cdot OH$, obtained from ethyl lactate by the Grignard method, crystallises in long needles and melts at 96·5°; the *diacetate* melts at 153°.

Diphenylacetone, $CHPh_2\cdot COMe$, obtained quantitatively from the preceding glycol and slightly acidified water at 180°, is dimorphous, the one form melting at 46°, the other at 61°. The less fusible substance has not been transformed into its isomeride, but both yield the same *oxime*, which melts at 164·5°, *semicarbazone*, which melts at 170°, and *phenylhydrazone*, which melts at 131°.

ββ-Di-p-*tolylpropylene aβ-glycol*, $OH\cdot C(C_7H_7)_2\cdot CHMe\cdot OH$, prepared in similar manner, melts at 67°, and when heated with acetic anhydride forms *di*-p-*tolylacetone*, $CH(C_7H_7)_2\cdot COMe$, which is also obtained by the direct distillation of the glycol; it boils at 194° under 20 mm. pressure. The *oxime* melts at 189°, the *semicarbazone* at 172°, and the *phenylhydrazone* at 122°. Di-*o*-tolylpropylene glycol is not obtained from magnesium *o*-tolyl bromide and ethyl lactate; when the reaction product is decomposed by ice and acetic acid, an oil is obtained from which a substance, apparently o-*tolualdehyde*, is obtained, together with *di*-o-*tolylacetone*, $CH(C_7H_7)_2\cdot COMe$, which is a viscous oil, boils at 198° under 12 mm. pressure, and does not form a sodium hydrogen sulphite compound. The *oxime* melts at 171°, the *semicarbazone* at 152°. C. S.

Unsymmetrical Diphenylethylene Oxide and Diphenylethylene Glycol. CARL PAAL and ERICH WEIDENKAFF (*Ber.*, 1906, **39**, 2062—2063. Compare Abstr., 1905, i, 436; this vol., i, 236).—*as*-Diphenylethylene oxide (Klages and Kessler, this vol., i, 498) may be obtained by the action of nitrous acid on diphenylaminomethylcarbinol. *as*-Diphenylethylene glycol, $OH\cdot CPh_2\cdot CH_2\cdot OH$, is readily prepared by the action of magnesium phenyl bromide on ethyl glycollate.

It crystallises from its aqueous solution in large, colourless needles, melting at 121°, and dissolves readily in most organic solvents.

J. J. S.

Optically Active 4-Methyl*cyclo*hexylidene-1-acetic Acid. Willy Marckwald and Richard Meth (*Ber.*, 1906, **39**, 2035—2038. Compare this vol., i, 360; Perkin and Pope, Proc., 1906, **22**, 107).—The acid previously described readily loses carbon dioxide, yielding a hydrocarbon, C_8H_4, already described by Wallach, and its products of oxidation prove it to be 1-methyl-4-methylene*cyclo*hexane. The constitution of the acid is therefore regarded as established.

The cinchonine salt, when pure, melts at 62—64°, and has $[\alpha]_D + 16 \cdot 0°$.

J. J. S.

Simple Method for the Synthesis of α-Amino-acids. Hans Bucherer (*Ber.*, 1906, **39**, 2033—2034).—Priority as against Zelinsky and Stadnikoff (this vol., i, 425) is claimed (compare Abstr., 1905, i, 438).

J. J. S.

Phenylbutyric Acids and their α-Amino-derivatives. Emil Fischer and Wilhelm Schmitz (*Ber.*, 1906, **39**, 2208—2215. Compare this vol., i, 182; Knoop and Hössli, *ibid.*, 431).—Chloroethylbenzene prepared by the action of chlorine on boiling ethylbenzene consists principally of the α-isomeride, as when boiled with copper nitrate solution it is oxidised to acetophenone, which is obtained in a yield of more than 60 per cent. of the theoretical. The following constitutions must therefore be ascribed to the derivatives of malonic and phenylbutyric acids previously described: *ethyl β-phenylethylmalonate*, $CHMePh \cdot CH(CO_2Et)_2$, instead of ethyl γ-phenylethylmalonate; *β-phenylethylmalonic acid*, $CHMePh \cdot CH(CO_2H)_2$, instead of γ-phenylethylmalonic acid; *α-bromo-β-phenylethylmalonic acid*,

$$CHMePh \cdot CBr(CO_2H)_2,$$

instead of α-bromo-γ-phenylethylmalonic acid; and *α-bromo-β-phenylbutyric acid*, $CHMePh \cdot CHBr \cdot CO_2H$, and *α-amino-β-phenylbutyric acid*, $CHMePh \cdot CH(NH_2) \cdot CO_2H$, instead of α-bromo- and α-amino-γ-phenylbutyric acids respectively. The terms *prim.*-phenethyl and *sec.*-phenethyl are used by the authors for the groups $CHPh \cdot CH_2$ and $CHMePh$ respectively.

The following derivatives of γ-phenylethylmalonic and γ-phenylethylbutyric acids have been prepared from Grignard's ω-bromoethylbenzene (Abstr., 1904, i, 213) in the same way as the β-phenyl compounds from α-chloroethylbenzene.

Ethyl γ-phenylethylmalonate, $CH_2Ph \cdot CH_2 \cdot CH(CO_2Et)_2$, is obtained as a colourless, viscid oil, which boils at 178—182° under 16 mm. pressure. The *acid*, $CH_2Ph \cdot CH_2 \cdot CH(CO_2H)_2$, crystallises from benzene in microscopic needles, or from hot water in sheaves of small, colourless, pointed needles, melts and evolves carbon dioxide at 130—131° (corr.), and when heated at 140° yields γ-phenylbutyric acid.

α-Bromo-γ-phenylethylmalonic acid, $CH_2Ph \cdot CH_2 \cdot CBr(CO_2H)_2$, crystallises from water in slender needles, melts and decomposes at 158°

(corr.), and when heated at 160—165° yields *a bromo γ phenylbutyric acid*, which is obtained as a viscid oil.

α-Amino-γ-phenylbutyric acid, prepared from the preceding bromo-acid, is identical with Knoop and Hössli's acid (*loc. cit.*). The *copper* salt forms a slightly blue, flocculent precipitate, which is only sparingly soluble in water.

β-Phenylbutyric acid, $CHMePh \cdot CH_2 \cdot CO_2H$, formed by heating β-phenylethylmalonic acid above its melting point, crystallises from water in small needles, or from light petroleum in small prisms, melts at 38—39° (corr.), and distils at 160° under 16 mm. or at 270° under the ordinary pressure. It forms a *calcium* salt, which separates from its aqueous solution when heated as a viscid oil, redissolving as the solution cools. The *lead* salt forms a white, amorphous precipitate; the *silver* salt, $C_{10}H_{11}O_2Ag$, forms slender needles. G. Y.

Stereoisomeric Cinnamic Acids. WILLY MARCKWALD and RICHARD METH (*Ber.*, 1906, **39**, 1966. Compare this vol., i, 360).—A reply to Erlenmeyer, jun., and Barkow (this vol., i, 429).

G. Y.

Derivatives of *o*-Nitromandelonitrile. GUSTAV HELLER and HEINRICH G. MAYER (*Ber.*, 1906, **39**, 2334—2339).—*o*-Nitromandelonitrile forms an *acetyl* derivative which melts at 52° and a *benzoyl* derivative which melts at 90—91°; the *amide*, $NO_2 \cdot C_6H_4 \cdot CH(OBz) \cdot CO \cdot NH_2$, of the latter melts at 128°. *Ethyl* o-*nitrobenzoylmandelate*,

$$NO_2 \cdot C_6H_4 \cdot CH(OBz) \cdot CO_2Et,$$

melts at 72°.

Benzoyldioxindole is obtained by reducing ethyl *o*-nitrobenzoylmandelate or the amide with stannous chloride and hydrochloric acid, and is identical with the substance obtained by benzoylating dioxindole (Abstr., 1904, i, 416).

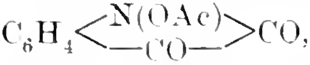
o-Nitrosobenzoic acid is the chief product formed when *o*-nitromandelonitrile is dissolved in alcoholic ammonia (compare *Ber.*, 1901, **34**, 948); the *methyl* ester, obtained by the use of methyl sulphate and sodium carbonate, melts at 152—153°, and when reduced yields methyl anthranilate. C. S.

A New Step in the Reduction of the Nitro-group. GUSTAV HELLER (*Ber.*, 1906, **39**, 2339—2346).—The first step in the reduction of the nitro-group is the formation of the group $N(OH)_2$. When *o*-nitromandelonitrile, dissolved in 33 per cent. acetic acid, is cooled to 0° and treated with zinc dust, a *substance* is obtained which crystallises in quadratic plates or leaflets, decomposes at 145°, and reduces solutions of gold, silver, and platinum salts. From its composition and behaviour, the substance is regarded as a quinhydrone-like compound, composed of $N(OH)_2 \cdot C_6H_4 \cdot CH(OH) \cdot CN,HCl$ and

$$OH \cdot NH \cdot C_6H_4 \cdot CH(OH) \cdot CN,HCl.$$

When heated on the water-bath with water and hydrochloric acid, about 40 per cent. of the substance is changed into o-*nitrosomandelonitrile*, $NO \cdot C_6H_4 \cdot CH(OH) \cdot CN$, which crystallises in colourless needles with a faint blue shade, melts at 210°, and is converted by boiling dilute alkali hydroxides into anthroxanic acid. When warmed with ferrous sulphate and sodium hydroxide and then acidified, the substance yields isatin, but if ammonia and ferrous sulphate are used, followed by sodium hydroxide, and the solution is then acidified and concentrated, isatyde is obtained.

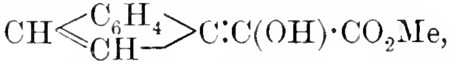
When the quinhydrone compound is warmed with hydrochloric acid, the second of the components mentioned above yields isatin.

By acetylation, the substance yields isatin and 1-*acetoxyisatin*,  $C_6H_4<\substack{N(OAc)\\ CO}>CO$, which separates from benzene in orange-red plates, melts at 151—152°, gives the indophenin reaction, and by solution in an alkali hydroxide, followed by the addition of excess of hydrochloric acid, yields anthroxanic acid.

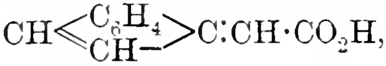
When 1-acetoxyisatin is treated with alcohol and phenylhydrazine, yellowish-green leaflets of 1-*hydroxyisatinphenylhydrazone*, $C_{14}H_{11}O_2N_3$, are obtained, which melt at 220°, but when it is warmed with excess of alcohol and phenylhydrazine, the *osazone*, $C_{20}H_{17}ON_5$, is formed, which crystallises in slender, yellow needles and melts at 169°. C. S.

Derivatives of Fulvene. II. Derivatives of Indeneoxalic Esters.

Johannes Thiele and Max Rüdiger (*Annalen*, 1906, **347**, 275—289. Compare this vol., i, 569; Thiele, Abstr., 1900, i, 347; Wislicenus, *ibid.*, 346).—In accordance with the strong colour of indeneoxalic esters, these are represented as the enolic form, in which they are derivatives of the strongly coloured fulvene.

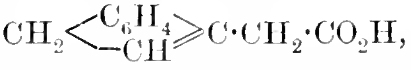
Methyl indeneoxalate,  $CH\ll\substack{C_6H_4\\ CH}>C{:}C(OH)\cdot CO_2Me$, formed with slight development of heat by the condensation of indene and methyl oxalate in presence of sodium ethoxide in absolute alcoholic solution, crystallises from benzene in orange-red needles and melts at about 90—92°, or at lower temperatures after repeated recrystallisation.

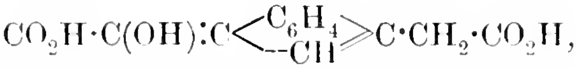
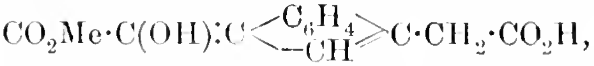
Ethyl α-hydroxyindeneacetate,  $CH\ll\substack{C_6H_4\\ CH}>CH\cdot CH(OH)\cdot CO_2Et$, prepared by reduction of ethyl indeneoxalate by means of aluminium amalgam and moist ether, is obtained as a yellow, viscid oil, which boils at 172° under 13 mm. pressure, and gives a deep red coloration with much concentrated sulphuric acid. It is readily hydrolysed by methyl-alcoholic or concentrated aqueous potassium hydrobromide, losing H_2O and forming *benzofulvenecarboxylic acid*,

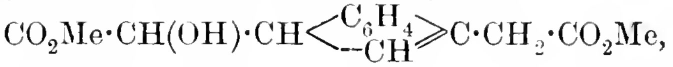


$$CH\ll\substack{C_6H_4\\ CH}>C{:}CH\cdot CO_2H,$$

which crystallises from benzene in microscopic, orange leaflets, commences to sinter at 175°, and when more highly heated partially sublimes and finally decomposes. With alcoholic potassium hydroxide, it gives a violet-red coloration, becoming green and then yellow on addition of water, and yields methylindene when distilled with soda-lime, or in a vacuum, or in a current of hydrogen. The *methyl* ester, $C_{12}H_{10}O_2$, crystallises in yellow needles, melts at 62—63°, and resembles quinone in appearance.

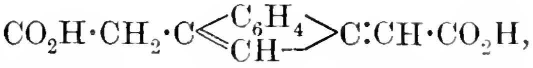
Indeneacetic acid,  $CH_2<\substack{C_6H_4\\ CH}>C\cdot CH_2\cdot CO_2H$, prepared by reduction of benzofulvenecarboxylic acid by means of aluminium amalgam, or zinc dust and ammonia, or of methyl benzofulvenecarboxylate by means of aluminium amalgam, crystallises in white needles, melts at 95—96°, remains unchanged when heated with 20 per cent. potassium hydroxide at 120° in a sealed tube, and yields methylindene when distilled with soda-lime. The *methyl* ester, $C_{12}H_{12}O_2$, is obtained as a yellow, viscid oil, which boils at 148—150° under 12 mm. pressure and solidifies partially when cooled by ice.

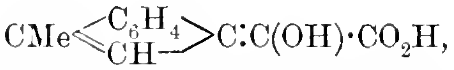
1-*Oxaloindene*-3-*acetic acid*,  $CO_2H\cdot C(OH){:}C{<}\begin{array}{c}C_6H_4\\ CH\end{array}{>}C\cdot CH_2\cdot CO_2H$, formed by hydrolysis of its esters, crystallises from dilute alcohol or acetic acid in orange-red needles, melts and decomposes at about 200°, and gives a brown to green coloration with ferric chloride. The *methyl hydrogen* ester,  $CO_2Me\cdot C(OH){:}C{<}\begin{array}{c}C_6H_4\\ CH\end{array}{>}C\cdot CH_2\cdot CO_2H$, prepared by the action of methyl oxalate on indeneacetic acid in presence of sodium methoxide in methyl-alcoholic solution, crystallises from chloroform in small, orange needles, or from a mixture of alcohol and chloroform in glistening leaflets, melts and decomposes at about 190°, and gives a transient, reddish-brown coloration with ferric chloride. The *dimethyl* ester, $C_{15}H_{14}O_5$, formed in the same manner from methyl indeneacetate and methyl oxalate, crystallises in yellow needles, melts at 109—110°, and gives with ferric chloride a similar coloration to the methyl hydrogen ester. When reduced with aluminium amalgam, it yields *dimethyl indene*-1-*acetate*-3-*a*-*hydroxyacetate*,



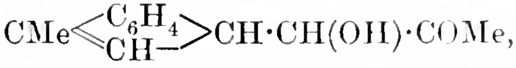
$$CO_2Me\cdot CH(OH)\cdot CH{<}\begin{array}{c}C_6H_4\\ CH\end{array}{>}C\cdot CH_2\cdot CO_2Me,$$

which is obtained as a yellow, viscid oil, giving a violet-red coloration with alcoholic potassium hydroxide.

Carboxybenzofulveneacetic acid,  $CO_2H\cdot CH_2\cdot C{<}\begin{array}{c}C_6H_4\\ CH\end{array}{>}C{:}CH\cdot CO_2H$, is formed by hydrolysis of the preceding ester by means of alcoholic potassium hydroxide; it crystallises from toluene in small, light yellow needles, melts and decomposes at 240—250°, and is reduced by zinc dust and ammonia, forming a colourless *acid* (*indenediacetic acid ?*).

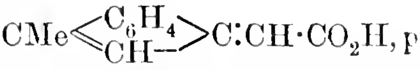
1-*Methylindene*-3-*oxalic acid*,  $CMe{<}\begin{array}{c}C_6H_4\\ CH\end{array}{>}C{:}C(OH)\cdot CO_2H$, is obtained by hydrolysis of its ester; it crystallises in slender, yellow needles, darkens and decomposes at about 200°, and gives a reddish-brown to green coloration with alcoholic ferric chloride, becoming colourless on addition of water. The *ethyl* ester, $C_{14}H_{14}O_3$, prepared from methylindene and ethyl oxalate, crystallises in orange-red needles, melts at about 92—94°, decomposes slowly at the ordinary temperature, and couples with diazobenzenesulphonic acid in acid or alkaline solution. The *methyl* ester, formed from methyl oxalate and methylindene, crystallises in hard, orange needles, melts at 135—136°, gives a transient, brown coloration with ferric chloride, and couples with diazobenzenesulphonic acid.

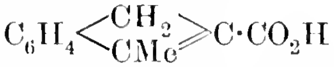
Methyl 1-*methylindene*-3-*a*-*hydroxyacetic acid*,



$$CMe{<}\begin{array}{c}C_6H_4\\ CH\end{array}{>}CH\cdot CH(OH)\cdot COMe,$$

formed by reduction of methyl methylindeneoxalate, is obtained as a yellow, viscid oil, which decomposes when distilled, and gives with alcoholic potassium hydroxide a cherry-red, with concentrated sulphuric acid a red solution with green fluorescence.

1-*Methylbenzofulvenecarboxylic acid*,  $CMe<\begin{smallmatrix}C_6H_4\\CH\text{--}\end{smallmatrix}>C{:}CH\cdot CO_2H$, prepared in the same way as benzofulvenecarboxylic acid, crystallises from benzene in orange needles and decomposes above 200°.

1-Methylindene-2-carboxylic acid,  $C_6H_4<\begin{smallmatrix}CH_2\\CMe\end{smallmatrix}>C\cdot CO_2H$ (Roser, Abstr., 1888, 1303), forms a *methyl* ester, $C_{12}H_{12}O_2$, which crystallises in white needles and melts at 78°, and an *ethyl* ester, $C_{13}H_{14}O_2$, which forms needles and melts at 38°. G. Y.

Gabriel's Conversion of Phthalides into Indanediones.

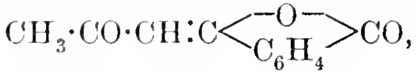
ALEXANDER EIBNER (*Ber.*, 1906, **39**, 2202—2204. Compare Nathanson, Abstr., 1894, i, 37).—Quinolylacetophenone-*o*-carboxylic acid is converted into the red sodium derivative of quinophthalone by sodium ethoxide, not directly, but if first heated with alcohol and a small quantity of concentrated hydrochloric or sulphuric acid. The reaction takes place therefore between sodium ethoxide and *ethyl quinolylacetophenone*-o-*carboxylate*, $C_{20}H_{17}O_3N$. This crystallises from light petroleum in yellow needles and melts at 250°.

The conversion of *as*-quinophthalone into its sodium derivative by the action of alcoholic sodium ethoxide takes place in two stages: the first is marked by the formation of a golden-yellow solution; the second, in which the red colour of the sodium derivative appears, takes place slowly at the ordinary temperature, but quickly on heating. The intermediate product is probably the above ester or its sodium derivative. G. Y.

Transformations of Phthalylacetylacetone.

CARL BÜLOW and MAX DESENISS (*Ber.*, 1906, **39**, 2275—2281. Compare Abstr., 1904, i, 610; 1905, i, 42, 529).—Phthalylacetylacetone is decomposed into acetylacetone and phthalic acid by boiling water; into phthalamide and phthalimide by alcoholic ammonia, and into methylphthalimide by 30 per cent. methylamine at 100°. A solution of sodium hydroxide in the cold, of sodium carbonate or hydrogen carbonate when warmed, and of barium hydroxide when boiled, decomposes phthalylacetylacetone into phthalic acid and acetylacetone.

The reaction between phthalylacetylacetone and ten times its weight of concentrated sulphuric acid yields *phthalylacetone*,



$$CH_3\cdot CO\cdot CH{:}C<\begin{smallmatrix}\text{—}O\text{—}\\C_6H_4\end{smallmatrix}>CO,$$

which separates from alcohol in white, feathery crystals and melts at 183°.

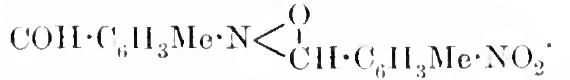
Phthalylacetylacetone is transformed by sodium methoxide into 2-acetyl-1 : 3-diketohydrindene, and is decomposed by hydrazine yielding β-phthalylhydrazine; by semicarbazine yielding *phthalylsemicarbazide*, $C_9H_7O_3N_3$, which melts at 249°; by *p*-nitrophenylhydrazine yielding *phthalyl*-p-*nitrophenylhydrazide*, $C_{14}H_9O_4N_3$, which melts at

247°. With hydroxylamine, the substance reacts normally, yielding *phthalylacetylacetone monoxime*, $C_{13}H_{11}O_4N$, which melts at 169°.

C. S.

Syntheses of Aromatic Aldehydes. I. LUDWIG GATTERMANN (*Annalen*, 1906, **347**, 347—386. Compare Gattermann and Koch, Abstr., 1897, i, 519; Gattermann and Frenzel, Abstr., 1898, i, 476; Gattermann and Berchelmann, *ibid.*, 581; Gattermann and Köbner, Abstr., 1899, i, 363; Gattermann and Maffezzoli, Abstr., 1904, i, 172).—The aldehydes described in this paper, which opens with a *résumé* of the author's three methods for the synthesis of aromatic aldehydes, have been prepared by the action of carbon monoxide and hydrogen chloride on hydrocarbons in presence of aluminium chloride and cuprous chloride.

Benzaldehyde is formed from benzene by this method only if aluminium bromide is substituted for the chloride. Dibenzylidenebenzidine melts at 234°, forming a liquid crystalline phase, changing to a clear liquid at 260°. The condensation products of other aromatic aldehydes with benzidine and substituted benzidines behave in the same manner.

When heated with concentrated hydriodic acid and red phosphorus in a sealed tube, *p*-tolualdehyde is reduced to *p*-xylene. Di-*p*-tolylidenebenzidine melts at 230°, forming a turbid liquid which becomes clear above the boiling point of sulphuric acid. Tolylideneazine melts at 158°; the phenylhydrazone melts at 112—113°. When reduced electrolytically in a mixture of glacial acetic acid and concentrated sulphuric acid with an *E.M.F.* of 5—6 volts and a current density of 1·2 amperes, *m*-nitro-*p*-tolualdehyde, which melts at 48—49° (43—44°, Hanzlik and Bianchi, Abstr., 1899, i, 597), yields the *compound*  $COH\cdot C_6H_3Me\cdot N<\begin{matrix}O\\ | \\ CH\cdot C_6H_3Me\cdot NO_2\end{matrix}$. This separates from benzene in yellow crystals, melts at 168°, and when oxidised with ferric chloride forms *nitroso*-p-*tolualdehyde*, $C_8H_7O_2N$, which crystallises in glistening, silvery needles and melts at 128°. 2 : 6-*Dinitro*-p-*tolualdehyde*, $C_6H_2Me(NO_2)_2\cdot COH$, formed by the action of a mixture of fuming nitric and concentrated sulphuric acids on *p*-tolualdehyde, crystallises in yellow needles, melts at 109°, and forms 2 : 6-dinitro-*p*-toluic acid when oxidised with potassium permanganate.

3 : 5-*Dinitro-4-methylbenzylidene chloride*, $C_8H_6O_4N_2Cl_2$, formed by nitration of 4-methylbenzylidene chloride, crystallises in large, colourless needles, melts at 90°, and when hydrolysed by means of a mixture of fuming and concentrated sulphuric acids yields 2 : 6-dinitro-*p*-tolualdehyde.

Ethyl p-*methylcinnamate*, $C_{12}H_{14}O_2$, prepared by the action of ethyl acetate and sodium on *p*-tolualdehyde, is obtained as a colourless, strongly refracting oil, which boils at 278°, has an odour resembling that of ethyl cinnamate, and on hydrolysis yields *p*-methylcinnamic acid. The ester reacts with bromine in carbon disulphide solution, forming *ethyl αβ-dibromo-4-methyldihydrocinnamate*, $C_{12}H_{14}O_2Br_2$, which crystallises from alcohol in large, glistening prisms and melts at 76·5°, together with an *oil*, probably a stereoisomeride. αβ-Dibromo-

4-methylcinnamic acid melts at 192° (183°, Kröber, Abstr., 1890, 968). On treatment with potassium hydroxide in hot concentrated alcoholic solution, the preceding ester yields *bromo-4-methylcinnamic acid*, $C_{10}H_9O_2Br$, which crystallises from benzene in white needles and melts at 192°. If in the preparation of this acid the filtrate from the potassium bromide is boiled in a reflux apparatus, the product is p-*tolylpropiolic acid*, $C_{10}H_8O_2$, which crystallises in long, colourless prisms, melts and decomposes at 148°, and when heated with aniline loses carbon dioxide, forming *p*-tolylacetylene.

m-Nitro-*p*-methylcinnamic acid melts at 173·5° (170—171°, Hanzlik and Bianchi, Abstr., 1899, i, 890).

p-Tolylideneacetone (Hanzlik and Bianchi, *loc. cit.*) distils at 142—145° under 15 mm. pressure as a strongly refracting oil. The *oxime*, $C_{11}H_{13}ON$, crystallises in colourless leaflets and melts at 126°. The *semicarbazone*, $C_{12}H_{15}ON_3$, forms colourless needles, becomes yellow on exposure to air, and melts at 202°. The *azine*, $C_{22}H_{24}N_2$, crystallises in yellow needles and melts at 190°. The phenylhydrazone forms yellow needles and melts at 154° (138°, Hanzlik and Bianchi, *loc. cit.*), and when heated above its melting point changes suddenly into *phenyl*-p-*tolylmethylpyrazoline*, $C_{17}H_{18}N_2$, which crystallises from light petroleum in colourless needles, melts at 112°, forms solutions with blue fluorescence, and gives Knorr's pyrazoline reaction. *m*-Nitro-*p*-tolylideneacetone is formed by nitration of *p*-tolylideneacetone.

Di-p-*tolylideneacetone*, $CO(CH{:}CH{\cdot}C_7H_7)_2$, is prepared by condensation of *p*-tolylideneacetone with *p*-tolualdehyde ; it crystallises from alcohol in glistening, slightly yellow needles, melts at 175°, with 2 mols. of hydrogen chloride in ethereal solution forms an unstable scarlet *hydrochloride*, and yields an *additive* compound with ferric chloride and hydrogen chloride.

Di-*p*-methylbenzoin (Stierlin, Abstr., 1889, 513) crystallises in triclinic prisms [$a : b : c = 0·593 : 1 : 0·282$; $\alpha = 126°51'44''$; $\beta = 116°45'2''$; $\gamma = 76°0'8''$].

Di-p-*methylbenzilic acid*, $C_{16}H_{16}O_3$, prepared by the action of aqueous potassium hydroxide on di-*p*-methylbenzil, crystallises in colourless needles, melts at 131°, and when heated at 150° forms an *anhydride*, $C_{32}H_{30}O_5$, which crystallises in colourless prisms and melts at 164°.

Hydro-p-*toluamide*, $N_2(CH{\cdot}C_7H_7)_3$, formed by the action of ammonia on *p*-tolualdehyde in cooled absolute alcoholic solution, crystallises in white needles, melts at 92°, and when heated at 130—140° for three to four hours, dissolved in alcohol, and treated with concentrated hydrochloric acid, is converted into *tri*-p-*methylamarine*, $C_{24}H_{24}N_2$. This crystallises from dilute acetone in colourless needles, melts at 127°, dissolves in alcohol, forming an alkaline solution, and becomes luminescent when heated with alcoholic potassium hydroxide at 70—75° in the dark. The *hydrochloride*, $C_{24}H_{25}N_2Cl$, crystallises in colourless needles and melts at about 295°. The *silver* derivative, $C_{24}H_{23}N_2Ag$, is formed as a white, amorphous precipitate. The *nitroso*-derivative, $C_{24}H_{23}ON_3$, forms yellow crystals and melts at 147°. When heated, hydro-*p*-toluamide yields ammonia, a polymeride of tolunitrile which melts above 260°, and trimethyl-lophine,

$C_{24}H_{22}N_2$. This crystallises from dilute alcohol in stout needles, melts at 234°, is a feeble base, and is more strongly luminescent than trimethylamarine when heated with alcoholic potassium hydroxide at 70°. The *acetate* crystallises in large octahedra, melts at 97°, and is decomposed by boiling alcohol.

3 : 4-*Dimethylbenzaldehyde*, $C_9H_{10}O$, formed from *o*-xylene, boils at 225°, and on oxidation yields 3 : 4-dimethylbenzoic acid. The *oxime*, C_9H_{10}:NOH, crystallises from light petroleum in colourless needles and melts at 69°. The *azine*, $N_2(C_9H_{10})_2$, separates from alcohol in sulphur-yellow leaflets and melts at 132°. The *phenylhydrazone*, $C_{15}H_{16}N_2$, forms colourless, unstable crystals and melts at 96°. The *condensation* product with *benzidine*, $C_{30}H_{28}N_2$, crystallises in golden-yellow leaflets and melts at 158° to a turbid, at 250° to a clear, liquid. The *trithioaldehyde*, $C_{27}H_{30}S_3$, forms colourless crystals and melts at 147°. 3 : 4-*Dimethylmandelic acid*, $C_{10}H_{12}O_3$, crystallises in glistening, colourless leaflets and melts at 105°. 3 : 4-*Dimethylcinnamic acid*, $C_{11}H_{12}O_2$, is formed by acting with malonic acid on 3 : 4-dimethylbenzylideneaniline, and heating the product with hydrochloric acid; it crystallises in colourless needles and melts at 142°. The *ethyl* ester, $C_{13}H_{16}O_2$, formed by the action of ethyl acetate and sodium on 3 : 4-dimethylbenzaldehyde, is obtained as a colourless, strongly refracting, pleasant-smelling oil which boils at 180—185° under 22 mm. pressure. 3 : 4-*Dimethylbenzylideneacetone*,

$$C_6H_3Me_2\cdot CH:CH\cdot COMe,$$

formed in the same way as tolylideneacetone, separates from ether in stout crystals, melts at 40°, and boils at 172° under 20 mm. pressure. The *semicarbazone*, $C_{13}H_{17}ON_3$, crystallises in colourless needles and melts at 207°.

2 : 4-Dimethylbenzaldehyde, formed from *m*-xylene, boils at 216—218° (compare Bouveault, Abstr., 1896, i, 649). The *oxime*, $C_9H_{11}ON$, crystallises in strongly refracting prisms and melts at 88°. The *phenylhydrazone*, $C_{15}H_{16}N_2$, forms colourless leaflets and melts at 88°.

5-*Nitro*-2 : 4-*dimethylbenzaldehyde*, $C_9H_9O_3N$, forms yellow needles, melts at 81°, and on oxidation yields 5-nitro-2 : 4-dimethylbenzoic acid. 2 : 4-*Dimethylmandelic acid*, $C_{10}H_{12}O_3$, crystallises from benzene in colourless needles and melts at 119°. 2 : 4-*Dimethylcinnamic acid*, $C_{11}H_{12}O_2$, formed by the action of malonic acid and alcoholic ammonia on the aldehyde, crystallises in glistening, colourless needles and melts at 181°. When reduced with sodium amalgam it yields 2 : 4-*dimethyldihydrocinnamic acid*, $C_{11}H_{14}O_2$, which crystallises in glistening, colourless leaflets and melts at 108°. 2 : 4-*Dimethylbenzylideneacetone*, $C_{12}H_{14}O$, forms yellow crystals, melts at 32°, and boils at 145—148° under 10 mm. pressure. The *semicarbazone*, $C_{13}H_{17}ON_3$, crystallises from alcohol in white needles and melts at 227°.

p-Xylene does not form an aldehyde, whilst 2 : 4 : 6-trimethylbenzaldehyde is formed from mesitylene in only small quantities by the carbon monoxide method.

2 : 4 : 5-Trimethylbenzaldehyde, formed from *ψ*-cumene, boils at 243°, is oxidised by potassium permanganate in dilute alkaline solution, forming durylic acid, and is reduced to durene by hydriodic acid and

red phosphorus. When exposed to direct sunlight, the colourless crystals of the aldehyde become yellow, changing again in the dark to the colourless state (compare Marckwald, Abstr., 1900, ii, 2). The *oxime*, $C_{10}H_{13}ON$, crystallises from light petroleum in colourless needles and melts at 102°. The *phenylhydrazone*, $C_{16}H_{18}N_2$, forms colourless leaflets and melts at 138°.

The nitration of ψ-cumylaldehyde, as also that of *p*-xylylaldehyde and of the corresponding acetophenones, leads to the formation of the *o*-nitro-derivatives as the main products, whilst the *m*-nitro-derivatives are formed at the same time in smaller amount.

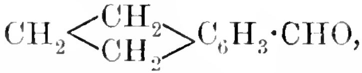
o-*Nitro-ψ-cumylaldehyde*, $C_{10}H_{11}O_3N$, formed best at -5° to -10°, crystallises in almost colourless leaflets, melts at 142°, and yields hexamethylindigotin when heated gently with acetone and alcoholic potassium hydroxide. When reduced, it forms o-*amino-ψ-cumylaldehyde*, $C_{10}H_{13}ON$, which crystallises in yellowish-green leaflets, melts at 102—103°, and is volatile in a current of steam. When diazotised and boiled with dilute sulphuric acid, this yields o-*hydroxy-ψ cumylaldehyde*, $C_{10}H_{12}O_2$, which crystallises from alcohol in colourless leaflets and melts at 78—79°.

o-*Nitrodurylic acid*, $C_{10}H_{11}O_4N$, formed by oxidation of the *o*-nitro-aldehyde with potassium permanganate, crystallises in colourless needles and melts at 192—193°. 6-*Nitro*-2 : 4 : 5-*trimethylcinnamic acid*, $C_{12}H_{13}O_4N$, formed by the action of sodium acetate and acetic anhydride on the *o*-nitro-aldehyde, crystallises from alcohol in slightly yellow leaflets and melts at 186—187°.

m-*Nitro-ψ-cumylaldehyde*, $C_{10}H_{11}O_3N$, crystallises from alcohol in long, colourless needles and melts at 128°. *Dinitro-ψ-cumylaldehyde*, $C_{10}H_{10}O_5N_2$, prepared by the action of potassium nitrate and concentrated sulphuric acid on the *o*-nitroaldehyde, crystallises from acetic acid in colourless needles and melts at 175°.

Cuminaldehyde is formed in good yield from cumene by the carbon monoxide method. The *azine*, $C_{20}H_{24}N_2$, crystallises in yellow needles and melts at 118°.

Diphenyl-4-*aldehyde*, $C_{13}H_{10}O$, prepared from diphenyl, crystallises from light petroleum, melts at 60—61°, and when oxidised by potassium permanganate yields diphenyl-4-carboxylic acid, which is reduced by hydriodic acid and red phosphorus, forming 4-methyldiphenyl. This crystallises in colourless leaflets and melts at 47—48° (Carnelly, this Journal, 1876, i, 13). The *oxime*, $C_{13}H_{10}\!:\!NOH$, forms colourless needles and melts at 149—150°; the *phenylhydrazone*, $C_{19}H_{16}N_2$, crystallises in slightly yellow needles and melts at 188—189°; the *aniline* derivative, $C_6H_4Ph\cdot CH\!:\!NPh$, crystallises in colourless leaflets and melts at 150—151°.



Hydrindene-5-aldehyde, $CH_2{<}\substack{CH_2\\CH_2}{>}C_6H_3\cdot CHO$, is formed in a 25 per cent. yield from hydrindene, together with an *oil* which has an odour of roses and boils at 168° under 18 mm. pressure, and a *substance*, $C_{17}H_{18}O$, which crystallises in colourless leaflets, melts at 83°, boils at 192° under 18 mm. pressure, is soluble in aqueous alkali hydroxides, and is precipitated from its alkaline solution by carbon dioxide.

The *aldehyde* forms a colourless oil which boils at 255—257°, and is oxidised by potassium permanganate, forming trimellitic acid, or slowly by air, forming *hydrindene-5-carboxylic acid*, $C_{10}H_{10}O_2$. This crystallises in microscopic prisms and melts at 177°. The aldehyde forms an *oxime*, $C_{10}H_{11}ON$, crystallising in colourless leaflets and melting at 65°; an *azine*, $C_{20}H_{20}N_2$, crystallising in yellow needles and melting at 162°; and an *aniline* derivative, $C_{16}H_{15}N$, crystallising in stellate aggregates of needles and melting at 85°. G. Y.

A New Reaction of Aldehydes. Action of *iso*Hydroxycarbamide on Benzaldehyde, and Properties of Benzylidenecarbamidoxime. Action of Water on Benzylidenecarbamidoxime.

A. CONDUCHÉ (*Bull. Soc. chim.*, 1906, [iii], **35**, 418—430 and 431—435).—Most of the data given in the first paper have been recorded already (Abstr., 1905, i, 288). The products of the action of hydrochloric acid on benzylidenecarbamidoxime are now given as benzonitrile and ammonium chloride (compare *loc. cit.*). It is also found that the product of the action of alcoholic or aqueous alkalis on benzylidenecarbamidoxime is α-benzaldoxime, and not the β-isomeride as previously supposed (*loc. cit.*). Potassium cyanate condenses immediately with β-benzaldoxime hydrochloride to form benzylidenecarbamidoxime. The same condensation product is formed when potassium cyanate reacts with α-benzaldoxime, but only in presence of nitric acid (compare *loc. cit.*).

In the second paper it is shown that when benzylidenecarbamidoxime is boiled with water or when heated in closed tubes with water at 120° or at 160—220° the same products are formed, namely, α-benzaldoxime, benzamide, benzonitrile, and carbamide, the relative proportions of these substances formed depending on the temperature employed.

T. A. H.

Action of Nitrogen Tetroxide on Benzaldoxime.

GIACOMO PONZIO (*J. pr. Chem.*, 1906, [ii], **73**, 494—496. Compare Beckmann, Abstr., 1889, 980; Scholl, Abstr., 1891, 315).—The action of 1 mol. of nitrogen tetroxide on 1 mol. of benzaldoxime in ethereal solution leads to the formation of benzaldoxime peroxide and diphenylglyoxime peroxide in yields of 15 per cent., and of phenyldinitromethane in a yield of 50 per cent. of the theoretical, whilst the action of 2 mols. of nitrogen tetroxide leads to the formation of phenyldinitromethane in a yield of 75 per cent. of the benzaldoxime, no peroxide being formed.

G. Y.

Phenylacetic Acid. Ketone Dyes. Trihydroxydeoxybenzoin and its Derivatives.

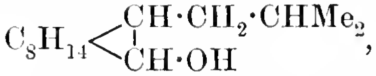
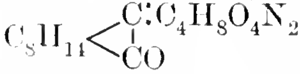
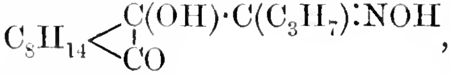
EMILIO NOELTING and VIKTOR KADIERA (*Ber.*, 1906, **39**, 2056—2060).—*Phenylgallacetophenone* (*trihydroxydeoxybenzoin*), $CH_2Ph\cdot CO\cdot C_6H_2(OH)_3$, obtained by heating together phenylacetic acid, pyrogallol, and zinc chloride at 150° for thirty minutes, crystallises from water, in which it is somewhat sparingly soluble, as pale yellow prisms melting at 141—142°. It dissolves readily in most organic solvents and in dilute potassium hydroxide, giving a yellow solution which turns red when heated. The *oxime*,

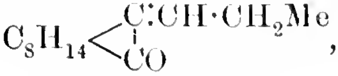
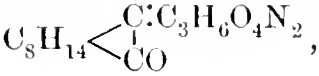
$$CH_2Ph\cdot C(NOH)\cdot C_6H_2(OH)_3,$$

crystallises in pale yellow needles melting at 166°. It dissolves sparingly in chloroform, and its solutions in alkali hydroxides are first yellow, but rapidly turn green. The isomeric iso*nitroso*-derivative, $OH\cdot N\colon CPh\cdot CO\cdot C_6H_2(OH)_3$, obtained by the action of nitrous acid on the ketone, crystallises from dilute alcohol in bright yellow cubes melting at 144° and soluble in hot water and most organic solvents.

The *di*iso*nitroso*-derivative, $OH\cdot N\colon CPh\cdot C(\colon N\cdot OH)\cdot C_6H_2(OH)_3$, forms colourless crystals melting at 168° and dissolves readily in alcohol or glacial acetic acid; when boiled with dilute hydrochloric acid, it yields *trihydroxybenzil*, $C_6H_5\cdot CO\cdot CO\cdot C_6H_2(OH)_3$, which crystallises from hot water in colourless needles melting at 143° and readily soluble in most solvents. J. J. S.

1 : 4-Anthraquinone. CARL LIEBERMANN (*Ber.*, 1906, **39**, 2089—2090).—A reply to Lagodzinski (this vol., i, 439). C. S.

The Products of the Action at a High Temperature of Sodium *iso*Butoxide or Propoxide on Camphor. ALBIN HALLER and JULES MINGUIN (*Compt. rend.*, 1906, **142**, 1309—1313. Compare Abstr., 1892, 72).—iso*Butylcamphol*,  $C_8H_{14}<\substack{CH\cdot CH_2\cdot CHMe_2\\ |\\ CH\cdot OH}$, obtained by heating sodium *iso*butoxide and camphor in an autoclave at 220—230° for twenty-four hours, forms opaque, white crystals, distils between 235° and 255°, melts at 55°, and has $[\alpha]_D$ +20·7° in alcoholic solution; the *acetate* boils at 135° under 20 mm. pressure. iso*Butylcamphor*,  $C_8H_{14}<\substack{CH\cdot CH_2\cdot CHMe_2\\ |\\ CO}$, obtained by oxidising *iso*butylcamphol by means of potassium permanganate, melts at 28°, and has $[\alpha]_D$ +72·4° in alcoholic solution. When heated with bromine in sealed tubes at 100° it yields iso*butylidenecamphor*,  $C_8H_{14}<\substack{C\colon CH\cdot CHMe_2\\ |\\ CO}$, an oily liquid which boils at 145° under 10 mm. pressure, has $[\alpha]_D$ +114·4°, and yields *iso*butyric and camphoric acids on oxidation. The *nitrosate*,  $C_8H_{14}<\substack{C\colon C_4H_8O_4N_2\\ |\\ CO}$, formed by the action of concentrated nitric acid or amyl nitrite and nitric acid, forms thin, white needles, melts with decomposition at 178°, is slightly soluble in alcohol and ether, more readily so in boiling benzene or acetone, and has $[\alpha]_D$ +93°. By the action of dilute potassium hydroxide it is converted into iso*nitroso-hydroxy*iso*butylcamphor*,  $C_8H_{14}<\substack{C(OH)\cdot C(C_3H_7)\colon NOH\\ |\\ CO}$, which crystallises from a mixture of ether and light petroleum in the form of thin, white needles melting at 95°.

Propylcamphol,  $C_8H_{14}<\substack{CHPr^{\alpha}\\ |\\ CH\cdot OH}$, prepared in similar manner to the corresponding *iso*butyl compound, crystallises from methyl alcohol, melts at 61°, and has $[\alpha]_D$ +12·5°; the *acetate* boils at 120° under 10 mm. pressure and solidifies at 0°. *Propylcamphor*,  $C_8H_{14}<\substack{CHPr^{\alpha}\\ |\\ CO}$, is a liquid which boils at 123° under 14 mm. pressure and has $[\alpha]_D$ +55·6°. *Propylidenecamphor*,  $C_8H_{14}<\begin{array}{l}C{:}CH\cdot CH_2Me\\ \mid\\ CO\end{array}$, is a liquid which has $[\alpha]_D$ +87° and has not yet been obtained quite pure, but which yields the *nitrosate*,  $C_8H_{14}<\begin{array}{l}C{:}C_3H_6O_4N_2\\ \mid\\ CO\end{array}$, melting and decomposing at 160°.

M. A. W.

Carvone. III. The Semicarbazones of Carvone. HANS RUPE and KARL DORSCHKY (*Ber.*, 1906, **39**, 2112—2115. Compare Abstr., 1905, i, 449; this vol., i, 374).—The carvone semicarbazone melting at 141—142° (Knoevenagel and Samel, this vol., i, 296) was obtained two years ago by the authors by adding to a concentrated aqueous solution of semicarbazide hydrochloride, carvone, alcohol, and finally potassium acetate, rise of temperature being carefully avoided; without this precaution and by using sodium hydrogen carbonate in the place of potassium acetate, the semicarbazone which melts at 162—163° (Baeyer, Abstr., 1894, i, 535) is obtained. Both forms are crystallographically identical and mutually convertible, the former changing completely into the latter by prolonged boiling in methyl-alcoholic solution or by careful heating at 170—175°; the latter isomeride is only partially converted into the former in boiling methyl alcohol, the complete transformation being observed only once in the case of a specimen which had been kept for a year. The two isomerides are soluble in the ordinary organic solvents, sparingly in the cold, easily on warming.

The isomeride with the higher melting point is unchanged in pyridine solution; the other changes sufficiently slowly to enable its rotatory power to be measured. The former has $[\alpha]_D$ 11·50° and the latter 11·30° at 20°. The specific rotation of the latter is constant for a short time, and then suddenly changes to another constant value about five minutes smaller.

[With WALTER HOTZ.]—The semicarbazones are monoclinic [$a:b:c = 0·50550:1:0·4706$; $\beta = 83°26'$]. C. S.

Aroma of Natural Musk. HEINRICH WALBAUM (*J. pr. Chem.*, 1906, [ii], **73**, 488—493).—When distilled with steam, crude musk yields 1·4 per cent. of a dark-brown oil, about half of which distils at 200—210° under 9 mm. pressure.

Muskone, $C_{15}H_{28}O$ or $C_{16}H_{30}O$, is obtained by treating the distillate with alcoholic potassium hydroxide and distilling the product at 160—164° under 7 mm. pressure. It is a colourless, viscid oil, which has a strong but pleasant odour of musk, boils at 142—143° under 2 mm., or with slight decomposition at 327—330° under 752 mm. pressure, has a sp. gr. 0·9268 at 15°, n_D 1·479 at 25° or 1·4844 at 15°, and $[\alpha]_D$ −10°6′. It is only sparingly soluble in water, but readily so in alcohol, does not form an additive compound with sodium hydrogen sulphite, and does not give a red coloration with rosaniline decolorised by sulphur dioxide.

The *oxime* crystallises in needles and melts at 46°. The *semi-*

carbazone, $C_{16}H_{31}ON_3$ or $C_{17}H_{33}ON_3$, crystallises in slender, white prisms, melts at 133—134°, and is odourless, but gives an odour of musk when heated with dilute sulphuric acid. Muskone is not identical with Bauer's ketone musk (Abstr., 1898, i, 523).

The fraction boiling at 65—106° under 7 mm. pressure, obtained in the purification of muskone, has an unpleasant odour and gives the pine-wood reaction for pyrrole. G. Y.

Copaiba Balsam from Surinam. LEOPOLD VAN ITALLIE and C. H. NIEUWLAND (*Arch. Pharm.*, 1906, **244**, 161—164. Compare Abstr., 1904, i, 1037).—The bulk of the resin is soluble in 5 per cent. aqueous sodium carbonate; the resin-*acid* has an acid number 171 and saponification number 178, and cannot be crystallised or separated into different acids by fractional precipitation of its salts. The *resen* cannot be crystallised.

From the sesquiterpene alcohol, which melts at 114—115° when purified, a *sesquiterpene* was obtained, of which the molecular weight corresponds with the formula $C_{15}H_{24}$; it is a mobile liquid which boils at 252° under 759 mm. pressure, has a sp. gr., 0·952 at 15°, n_D 1·5189 at 15°, and $[\alpha]_D - 61{\cdot}7°$; in the air, it soon changes to a resinous solid. C. F. B.

Formula of Elaterin. ARMAND BERG (*Bull. Soc. chim.*, 1906, [iii], **35**, 435—437. Compare Abstr., 1898, ii, 447).—Elaterin has the formula $C_{28}H_{38}O_7$, yields a *diacetyl* derivative, and on hydrolysis with potassium hydroxide in alcohol furnishes acetic acid (1 mol.) and *elateridin*. The latter, by the further action of the alkali, yields *elateric acid*. These products are all amorphous and non-volatile. T. A. H.

Curcumin. C. LORING JACKSON and LATHAM CLARKE (*Ber.*, 1906, **39**, 2269—2270. Compare Abstr., 1905, i, 804).—As a result of Zeisel determinations with curcumin, it is concluded that the formula for curcumin is $C_{14}H_{14}O_4$, and not $C_{21}H_{20}O_6$, that assigned to it by Ciamician and Silber. A. McK.

Condensation of Gallocyanin Dyes with Aminosulphonic Acids. EUGÈNE GRANDMOUGIN (*Zeit. Farb. Ind.*, 1906, **5**, 201).—Gallocyanin dyes condense with aminosulphonic acids, when warmed with them in aqueous suspension, to form dyes which are bluer in colour than the original substances; the condensation of prune (Sandoz) with sulphanilic acid is described in detail. Naphthionic acid, *o*-toluidinesulphonic acid, *p*-toluidinesulphonic acid, and *ββ*-naphthylaminesulphonic acid can be used in place of sulphanilic acid, but dimethylmetanilic acid does not condense with the dyes, a free amino-radicle apparently being essential for the condensation. W. A. D.

Tannins. EDUARD STRAUSS and BERNHARD GSCHWENDNER (*Zeit. angew. Chem.*, 1906, **19**, 1121—1125).—*Quebracho tannin*,

$$[C_{41}H_{44}O_{18}(OMe)_2]_2,$$

was obtained from the bark of *Quebracho colorada* by extracting first with chloroform and then with alcohol. On adding water to the alcoholic extract and warming, phlobaphens are deposited from the solution, which are then removed by shaking the solution with Tripoli powder. On concentrating the solution in a vacuum, the tannin was precipitated by means of lead acetate, the lead salt after filtration being then suspended in water and decomposed with hydrogen sulphide. The aqueous solution so obtained was then evaporated in a vacuum, and the residue taken up in the least amount of alcohol and poured into absolute ether. By this means, the tannin was obtained in the form of light flakes which were rapidly dried in a vacuum over sulphuric acid and phosphoric oxide; it at once becomes sticky on exposure to moist air. Analyses agreed with the formula $C_{43}H_{50}O_{20}$, which is the formula given by Schuett to the tannin from quinine.

By heating the tannin with a mixture of acetic anhydride and glacial acetic acid, an *acetyl* derivative is obtained, which, however, has the formula $(C_{30}H_{22}O_{11}Ac_6)_2$, forms a white powder which is fairly readily soluble in alcohol, very soluble in acetone, ethyl acetate, glacial acetic acid, or acetic anhydride, but is insoluble in water, ether, or benzene. The corresponding *benzoyl* derivative, $(C_{30}H_{22}O_{11}Bz_6)_2$, is a white solid; it darkens at 200° and decomposes at 215°. An aqueous solution of the tannin allowed to remain for two days with a solution of formaldehyde deposited a dark red substance which could not be further purified. When reduced with sodium amalgam, the tannin yields a compound of the formula $(C_{30}H_{28}O_{11})_2$.

Maletto tannin, $(C_{43}H_{50}O_{20})_2$, was obtained from finely-powdered Maletto bark by extraction with 96 per cent. alcohol. From its analysis and properties it appears to be identical with Quebracho tannin.

Tannin from tea, $(C_9H_{10}O_5)_x$, was obtained from finely-powdered black tea by first extracting it with chloroform and then with alcohol, and proceeding with the extraction and purification already described. It forms an almost white powder. If lead acetate is used in the purification, a compound of the formula $C_{13}H_{19}O_{10}$ is obtained.

Sumach tannin, $(C_{16}H_{15}O_{11})_x$, was prepared according to Loewe's instructions. A determination of methoxyl showed that the formula should be $C_{32}H_{29}O_{11}{\cdot}OMe$. P. H.

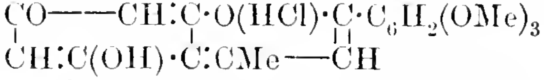
Iodotannin. VIGNERON (*J. Pharm. Chim.*, 1906, [vi], 23, 469—471).—A two per cent. solution of tannin in water to which one per cent. of iodine has been added gives a brown precipitate with sodium hydrogen carbonate, a red coloration with potassium cyanide, a red coloration, slight precipitate, and free iodine on addition of nitric acid containing nitrous acid, and when this is followed by potassium cyanide, the red coloration changes to yellow, and a thick, white precipitate is formed.

A similar solution of iodogallic acid gives a black precipitate with sodium hydrogen carbonate, and no precipitate on the addition of nitric acid containing nitrous acid, and followed by potassium cyanide. The reaction with potassium cyanide alone is similar to that with the iodotannin solution. The author is of opinion that iodotannin extracts recently sold in France for making galenical preparations are prepared from gallic acid and not from tannin. T. A. H.

Formation of Methronic Acid. GEORG SCHROETER (*Ber.*, 1906, 39, 2129—2131).—A claim for priority and a criticism of Trephilieff's views regarding the mechanism of the formation of methronic acid (this vol., i, 528). A. McK.

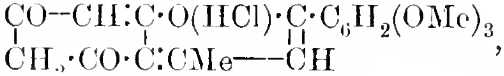
Quinonoid Benzopyran Derivatives. CARL BÜLOW and CARL SCHMID (*Ber.*, 1906, 39, 2027—2033. Compare this vol., i, 201, 300).

Phloroglucinol condenses with 2 : 3 : 4-trimethoxybenzoylacetone in the presence of hydrogen chloride in acetic acid solution, yielding *5-hydroxy-7-keto-2*-o-m-p-*trimethoxyphenyl-4-methyl*-1 : 4-*benzopyran hydrochloride*,



$$\begin{array}{l}\mathrm{CO{-\!\!-\!\!-}CH{:}C{\cdot}O(HCl){\cdot}C{\cdot}C_6H_2(OMe)_3}\\ \mathrm{CH{:}C(OH){\cdot}C{:}CMe{-\!\!-}CH}\end{array}$$

or



$$\begin{array}{l}\mathrm{CO{-}CH{:}C{\cdot}O(HCl){\cdot}C{\cdot}C_6H_2(OMe)_3}\\ \mathrm{CH_2{\cdot}CO{\cdot}C{:}CMe{-\!\!-}CH}\end{array},$$

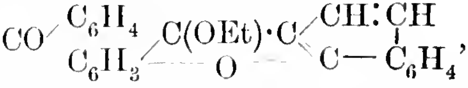
which crystallises from alcohol containing a small amount of hydrogen chloride in long, dark yellow needles containing $1H_2O$. The salt is partially hydrolysed in aqueous solution, and melts and decomposes at 218—219°. The *sulphate*, $C_{19}H_{18}O_6,H_2SO_4,C_2H_6O$, melts at 216—217°; the alcohol of crystallisation is removed by prolonged heating at 100°. When crystallised from alcohol containing 25 per cent. of sulphuric acid, a *sulphate*, $C_{19}H_{18}O_6,2H_2SO_4$, which crystallises in orange needles melting at 155—156°, is obtained. The *picrate*, $C_{25}H_{21}O_{13}N_3$, forms orange needles, changes colour at 100°, and melts and decomposes at 219—220°. The *base*, $C_{19}H_{18}O_6,H_2O$, forms small, brownish-red needles, softens at 140—145°, and is insoluble in ether and only sparingly soluble in benzene. It cannot be acetylated, but yields an *oxime*, $C_{19}H_{19}O_6N$, melting at 132—136°, and a *phenylhydrazone*, $C_{31}H_{30}O_4N_4$, which crystallises from alcohol in plates and melts at 113—114°.

When the hydrochloride is heated with concentrated hydrochloric acid at 150—180°, it yields *5-hydroxy-7-keto-2*-o-m-p-*trihydroxyphenyl-4-methyl*-1 : 4-*benzopyran hydrochloride*, $C_{16}H_{12}O_6,H_2O,HCl$, in the form of flesh-red, flat needles melting at 288°. The corresponding *base*, $C_{16}H_{12}O_6$, crystallises in dark brown, slender needles with a green lustre; it does not melt below 300°, and is insoluble in ether or benzene. J. J. S.

Benzocœroxonium Compounds. EDUARD LAUBE (*Ber.*, 1906, 39, 2245—2249).—*Erythroxyanthraquinone α-naphthol ether* [1-*α-naphthoxyanthraquinone*], $C_{24}H_{14}O_3$, prepared by heating a mixture of potassium anthraquinone-1-sulphonate and potassium α-naphthoxide for eight hours at 150—160°, separates from light petroleum in yellow crystals and melts at 275—276°. When warmed with concentrated sulphuric acid, it forms a purple solution.

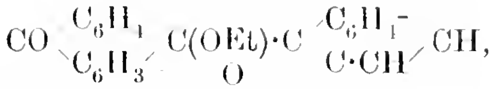
1-*β-Naphthoxyanthraquinone*, prepared in an analogous manner, forms a violet-red solution with concentrated sulphuric acid.

α-Benzocœroxonium ethyl ether,



pre-pared by heating 1-*α*-naphthoxyanthraquinone with 70 per cent. sulphuric acid at 150°, separates from alcohol in colourless leaflets and melts at 197—198°. The *ferrichloride*, $C_{21}H_{13}O_2Cl,FeCl_3$, of the base decomposes at 240°.

β-Benzoceroxonium ethyl ether,



$CO\left<\begin{matrix}C_6H_4\\C_6H_3\end{matrix}\right>\underset{O}{C(OEt)\cdot C}\left<\begin{matrix}C_6H_4-\\C\cdot CH\end{matrix}\right>CH$,

melts at 193—194 . The *ferrichloride* of the corresponding base melts at 240°.

Acetyl-α-benzoceroxenol, $C_{26}H_{16}O_3$, prepared by reducing benzoceroxonium salts by zinc dust and glacial acetic acid and then acetylating the product, separates from alcohol in yellow crystals. *Acetyl-β-benzoceroxenol* is brownish-yellow and melts at 195—200°.

By further reducing the benzoceroxenol compounds with hydriodic acid a small amount of *benzoceroxene* is obtained with other products.

A. McK.

Aconitine and Aconine from Aconitum Napellus. HEINRICH SCHULZE (*Arch. Pharm.*, 1906, **244**, 136—159, 165—196).—The first seventeen pages contain an historical account of previous researches. The results of the present research have already been published in part (Abstr., 1905, i, 656).

Purified aconitine, melting at 197—198° and identical in crystalline form with that analysed by Dunstan and Ince (Trans., 1891, 278—281), was found to have a composition corresponding, not with the formula proposed by these investigators or with that of Wright, but with those proposed by Freund and Beck, $C_{34}H_{47}O_{11}N$ or $C_{34}H_{45}O_{11}N$ (Abstr., 1894, i, 263). The hydrobromide was obtained crystallised from a mixture of alcohol and ether with $\frac{1}{2}H_2O$, when it melted and decomposed at 206—207°, and also crystallised with $2\frac{1}{2}H_2O$; the α-aurichloride, melting at 136·5°, crystallised with $3H_2O$. Aconitine is best hydrolysed by heating with water in an autoclave under 6—7 atmospheres pressure; the yield of aconine hydrochloride was 85 per cent. of the theoretical.

The tetra-acetyl derivative of picraconitine (benzoylaconine) is not different from the triacetyl derivative of aconitine (acetylbenzoylaconine), as Dunstan and Carr thought (Trans., 1895, 461, 462); the two substances melt at 207—208° and are identical. Aconine does not form a quaternary ammonium salt with methyl iodide or sulphate, or an amino-oxide with hydrogen peroxide. Aconine hydrochloride and hydrobromide, melting at 175—176° and 225°, were obtained crystallised with 2 and $1\frac{1}{2}H_2O$ respectively.

When aconitine is heated with methyl alcohol at 120—130°, the acetyl group is eliminated as acetic acid, but instead of picraconitine *methylpicraconitine* is obtained; the *hydrobromide* and *hydrochloride* of this crystallise each with $3H_2O$ and melt at 188—189° and 190° respectively; the base, which also is crystalline, is hydrolysed to aconine, benzoic acid, and methyl alcohol when it is heated with a large excess of water at 150—160° for twenty-four hours, the hydrolysis taking place much less readily than in the case of aconitine, where heating for six hours suffices. When aconitine is heated with ethyl alcohol, ethylpicraconitine is formed, but in worse yield than methylpicraconitine.

Aconine hydrobromide crystallises with $1\frac{1}{2}H_2O$, and melts and decomposes at about 225°. With bromine, the alkaloid forms a perbromide, but no addition or substitution product. Neither aconine nor aconitine, nor the tetra-acetyl derivative of the latter, decolorises potassium permanganate rapidly in dilute sulphuric acid solutions.

Alkaline permanganate or chromic acid oxidises aconine with formation of aldehyde, and, in the latter case, of methylamine. In the former case, the main product was amorphous. In the latter case, the main product, which was both acid and basic, could not be obtained crystalline; a portion had basic properties, and from this a crystalline hydrochloride, $C_{24}H_{35}O_8N,HCl$ (or $C_{24}H_{37}O_8N,HCl$), with $3H_2O$, melting at 213°, was obtained. C. F. B.

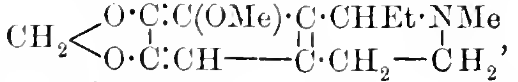
Old Decomposed Cocaine Hydrochloride. Pierre Breteau (*J. Pharm. Chim.*, 1906, [vi], **23**, 474—476).—In a sample, obviously decomposed, of this alkaloidal salt made in 1891, methyl benzoate, benzoic acid, and ecgonine hydrochloride were found. The decomposition is attributed to the presence of a small quantity of water in the original salt. T. A. H.

Derivatives of Caffeine and Reactions of its Glyoxaline Nucleus. Brissemoret (*Bull. Soc. chim.*, 1906, [iii], **35**, 316—321). —When a mixture of caffeine and salicylic acid in molecular proportions is dissolved in boiling water, there separates on cooling colourless, acicular crystals of the *compound* $C_8H_{10}O_2N_4,C_7H_6O_3$. An analogous *product* is obtained with protocatechuic or gallic acid.

Similar *compounds* may be obtained of 3 : 7-dimethylxanthine and gallic and salicylic acids and of 1 : 3-dimethylxanthine and gallic acid.

All these compounds dissolve on adding sodium hydroxide to their suspensions in water, and the bases may be then either filtered out or dissolved out by an appropriate solvent. It is possible to determine their composition by this means. The author regards the formation of these compounds as due to the influence of the glyoxaline ring in caffeine, and as evidence for the accuracy of this view points out that similar *combinations* may be brought about between glyoxaline itself and gallic or salicylic acid and that each of these may be isolated in a crystalline condition by mixing a solution of the base in ether with a like solution of the appropriate acid. T. A. H.

Behaviour of Cotarnine towards Grignard's Reagent. Martin Freund and Hans Hermann Reitz (*Ber.*, 1906, **39**, 2219—2237. Compare Abstr., 1904, i, 187).—1-*Ethylhydrocotarnine*,



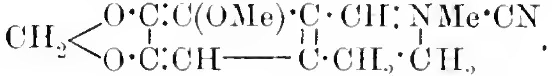
$$CH_2<\begin{array}{l} O\cdot C{:}C(OMe)\cdot C\cdot CHEt\cdot NMe \\ O\cdot C{:}CH\text{———}C\cdot CH_2\text{—}CH_2 \end{array}$$

prepared by the action of magnesium ethyl iodide on cotarnine, separates from dilute alcohol in rhombic pyramids and melts at 59—60°. Its *hydrochloride* crystallises in needles and melts at 215—216°; its *dichromate* crystallises in rhombic plates, whilst its *methiodide* separates from alcohol in hexagonal plates and melts at 188—189°. The 5-*bromo* derivative, $C_{14}H_{18}O_3NBr$, separates from light petroleum in octagonal plates and melts at 104°; the orientation of the bromine atom as indicated is correct, since the same compound is formed when magnesium ethyl iodide acts on bromocotarnine. When α-ethylcotarnine is oxidised with hydrogen peroxide, it is converted into the corresponding amino-oxide, the *platinichloride* of which,

$$(C_{14}H_{19}O_4N)_2,H_2PtCl_6,$$

forms tetragonal plates and melts at 196—197°.

Attempts to prepare methoxyl derivatives of benzyl α-hydrocotarnine by the action of magnesium alkyl halides on cyanocotarnine failed; when magnesium ethyl iodide, for example, acts on cyanocotarnine, ethyl hydrocotarnine is produced, a result which indicates that the probable formula for cyanocotarnine is



$$CH_2{<}\begin{array}{l} O{\cdot}C{:}C(OMe){\cdot}C{\cdot}CH{:}NMe{\cdot}CN \\ O{\cdot}C{:}CH\text{———}C{\cdot}CH_2{\cdot}CH_2 \end{array}.$$

1-*Propylhydrocotarnine*, $C_{15}H_{21}O_3N$, prepared by the action of magnesium propyl iodide on cotarnine, separates from light petroleum in tetragonal pyramids and melts at 66—67°. Its *hydriodide*,

$$C_{15}H_{31}O_3N,HI,$$

forms rhombic plates and melts at 165—166°. Its *methiodide*,

$$C_{15}H_{31}O_3N,MeI,$$

separates from alcohol in tetragonal crystals and melts at 165—166°.

1-iso*Propylhydrocotarnine hydriodide*, $C_{15}H_{31}O_3N,HI$, separates from alcohol in rhombic plates and melts at 196—197°. α-iso*Propylhydrocotarnine methiodide* separates from alcohol in needles and melts at 144—145°.

1-iso*Butylhydrocotarnine*, $C_{16}H_{23}O_3N$, separates from light petroleum in tetragonal pyramids and melts at 46—47°. Its *hydrochloride* separates from water in octagonal crystals and melts at 217—218°; its *platinichloride* melts and decomposes at 208—209°; its *hydrobromide* melts at 205—206°; its *methiodide* separates from alcohol in hexagonal plates and melts at 189—190°.

When 1-methylhydrocotarnine is oxidised by hydrogen peroxide, it forms an amino-oxide, the *platinichloride* of which,

$$(C_{13}H_{17}O_4N)_2,H_2PtCl_6,$$

crystallises from dilute alcohol in plates and melts at 198°, whilst the corresponding *hydriodide* melts at 116°.

1-*Phenylhydrocotarnine*, $C_{18}H_{19}O_3N$, prepared from magnesium phenyl iodide and cotarnine cyanide, separates from light petroleum in pyramids and melts at 97—98°. It may also be prepared from cotarnine hydrochloride and magnesium phenyl iodide.

1-p-*Methoxylphenylhydrocotarnine*, $C_{19}H_{21}O_4N$, is a viscid oil.

1-α-*Naphthylhydrocotarnine*, $C_{22}H_{21}O_3N$, melts at 120—122°; its *hydrobromide* separates from dilute alcohol in cubes and melts at 253°.

1-*Benzylhydrocotarnine*, $C_{19}H_{21}O_3N$, separates from light petroleum in rhombic plates and melts at 70°. Its *hydriodide* separates from alcohol in plates and melts at 217—218°.

Di-hydrocotarnine,

$$CH_2{<}\begin{array}{l} C_6H(O_2{:}CH_2)(OMe) \\ CH_2\text{———}NMe \end{array}{>}CH{\cdot}CH{<}\begin{array}{l} C_6H(O_2{:}CH_2)(OMe) \\ NMe\text{———}CH_2 \end{array}{>}CH_2,$$

prepared by the action of magnesium acetylene tetrabromide on cotarnine, crystallises from water in rhombohedra and melts at 163—164°. The *hydrobromide*, $C_{24}H_{28}O_6N_2,2HBr,2H_2O$, crystallises from water in rhombic needles and, when dehydrated, melts at 233—234°; the *hydrochloride*, $C_{24}H_{28}O_6N_2,2HCl,2H_2O$, separates from water in silky, rhombic leaflets and melts at 231—232°; the *hydriodide*, $C_{24}H_{28}O_6N_2,2HI$, separates from alcohol in needles and melts at 234—235°. The *hydrogen sulphate*, $C_{24}H_{28}O_6N_2,2H_2SO_4,2H_2O$, crystallises from water in pyramids and melts and decomposes at 236—237°; the *methiodide*, $C_{24}H_{28}O_6N_2,MeI$, crystallises from water in needles and melts at 233—234°.

Di-hydrocotarnine may also be obtained by the action on cotarnine of the magnesium compounds of alkyl iodides, methylene chloride, benzylidene chloride, ethylene bromide, and piperonyl chloride respectively.

p-*Cyanobenzyl iodide*, prepared by the action of potassium iodide on *p*-cyanobenzyl chloride, separates from alcohol in needles and melts at 143—144°. It does not form a magnesium compound.

The physiological action of a number of the compounds described has been tested. A. McK.

Conversion of Ephedrine into ψ-Ephedrine. ERNST SCHMIDT

(*Arch. Pharm.*, 1906, **244**, 239—240. Compare Abstr., 1904, i, 769).—A much better yield of ψ-ephedrine is obtained by heating ephedrine hydrochloride with ten times its weight of 25 per cent. hydrochloric acid for twelve hours in the water-bath. Even then the conversion is not complete; it seems that equilibrium is reached between the two substances. C. F. B.

Tetrathiocyanodipyridinechromium Salts. PAUL PFEIFFER and W. OSANN

(*Ber.*, 1906, **39**, 2115—2125).—*Pyridinium tetrathiocyanodipyridinechromiates.*—When dry potassium or ammonium chromothiocyanate is heated on the water-bath with anhydrous pyridine for four hours, a *substance* is obtained which separates from a small quantity of hot pyridine in glistening, dark red, prismatic crystals, stable in the air; it corresponds with the formula

$$Cr(SCN)_3,HSCN,4C_5NH_5,$$

but does not give a coloration with ferric chloride. At 100° it loses 1 mol. C_5NH_5, yielding a *substance*, $Cr(SCN)_3,HSCN,3C_5NH_5$, which again takes up 1 mol. C_5H_5N by crystallisation from this solvent. Sand and Burger's formula (this vol., i, 487) is rejected, and arguments are advanced in favour of regarding the substance

$$Cr(SCN)_3,HSCN,3C_5NH_5$$

as the normal additive compound of 1 mol. C_5H_5N and the acid $[Cr(C_5NH_5)_2(SCN)_4]H$; the substance $Cr(SCN)_3,HSCN,4C_5NH_5$ is regarded as belonging to the class of the anomalous ammonium salts (compare Werner, Abstr., 1903, i, 234). When either of the compounds suspended in cold water is treated with chlorine, a *dihydroxylochloride*, $[Cr(C_5NH_5)_2(OH_2)_2(OH)_2]Cl$, is obtained; potassium hydroxide eliminates the pyridine, and by subsequent treatment with concentrated hydrochloric acid pure tetra-aquodipyridinechromium chloride is obtained.

Potassium tetrathiocyanodipyridinechromiate,

$$Cr(C_5NH_5)_2(SCN)_4]K,2H_2O,$$

is the chief product of the reaction between anhydrous pyridine and potassium chromothiocyanate; after crystallisation from hot water, it is obtained as a stable, red powder. It can also be crystallised from aniline or quinoline, does not react with ferric chloride, and is decomposed by chlorine in the presence of cold water with the formation, ultimately, of tetra-aquodipyridinechromium chloride. When the dried substance is crystallised from pyridine, an additive *compound*, $[Cr(C_5NH_5)_2(SCN)_4]K,4C_5NH_5$, is obtained in the form of transparent, red crystals, which quickly effloresce in air, but not in an atmosphere of pyridine. Sodium chromothiocyanate yields similar compounds, $[Cr(C_5NH_5)_2(SCN)_4]Na,3H_2O$ and $[Cr(C_5NH_5)_2(SCN)_4]Na,4C_5NH_5$.

The $4C_5NH_5$ in these additive compounds is regarded as being in combination with the alkali metal (compare Rosenheim and Löwenstamm, Abstr., 1903, i, 325). C. S.

Halogen Compounds of Molybdenum and Tungsten. II. Arthur Rosenheim and Morduch Koss (*Zeit. anorg. Chem.*, 1906, 49, 148—156. Compare Abstr., 1905, ii, 717; Weinland and Knoll, Abstr., 1905, ii, 323; Sand and Burger, Abstr., 1905, i, 923; Hofmann and von der Heide, Abstr., 1896, ii, 605).—When molybdenum trioxide, MoO_3, is added in excess to a 10 per cent. aqueous solution of thiocyanic acid and the mixture boiled and filtered, a deep red solution is obtained, from which, on the careful addition of pyridine,

$$Mo(OH)_2(SCN)_3,2C_5H_5N$$

can be isolated in the form of brownish-red needles. It is thus shown that, contrary to the generally accepted view, sexavalent molybdenum can be reduced to the quinquevalent state by boiling with thiocyanic acid alone. The corresponding *quinoline* compound,

$$Mo(OH)_2(SCN)_3,2C_9H_7N,$$

prepared in an analogous manner, crystallises from absolute alcohol in dark, reddish-brown needles. From a solution of the pyridine compound in excess of thiocyanic acid, the *compound*,

$$H_2Mo(OH)_2(SCN)_5,C_5H_5N,$$

was obtained in black, lustrous, rhombic crystals, readily decomposed by water.

When either of the pyridine compounds is boiled with concentrated hydrogen chloride until all the thiocyanic acid is driven off, dipyridinepentachloromolybdite, $H_2MoCl_5,2C_5H_5N$, is obtained in light green needles. The three *bromides*, $H_2Mo(OH)_2Br_5,2C_5H_5N,2H_2O$, $HMo(OH)_2Br_4,C_5H_5N$, and $H_2Mo(OH)_2Br_5,2C_9H_7N$, recently described by Weinland and Knoll (*loc. cit.*), were also prepared and analysed; the formulæ ascribed to them differ slightly from those found by their discoverers.

Concentrated hydriodic acid exerts a reducing action on both the pyridine and quinoline compounds; from the respective solutions the *compounds* $H_5Mo_2I_{13},5C_5H_5N$ and $H_3Mo_2OI_9,3C_9H_7N$, containing quadrivalent molybdenum, were isolated in the form of black, lustrous needles.

From an aqueous solution of the compound

$$Mo(OH)_2(SCN)_3,2C_5H_5N$$

and excess of potassium cyanide, a *compound*, $K_5Mo(OH)_2(CN)_8$, was obtained in yellow plates. With a large excess of potassium cyanide, the *compounds* $K_4MoO_2(CN)_4,10H_2O$, in violet-red crystals, and $K_4MoO_2(CN)_4,5H_2O$, already described by Hofmann and von der Heide (*loc. cit.*), were obtained, as well as a new *compound*,

$$K_3Mo(OH)_2(CN)_5,$$

which forms deep blue needles. G. S.

Quinoline Hydrochloride. Action of Acid Chlorides on Quinoline. Oskar Eckstein (*Ber.*, 1906, **39**, 2135—2138).—Quinoline hydrochloride, prepared by the action of benzoyl chloride or of acetyl chloride on quinoline in the presence of traces of water, has the formula $(C_9NH_7,HCl)_2,H_2O$, the melting point of which agrees with that recorded in the literature, namely, 94°; *anhydrous quinoline hydrochloride*, however, melts at 134°, whilst its *platinichloride* forms prisms and melts at 227·5°. Its *hydrogen chloride additive compound*, $(C_9NH_7,HCl)_2,HCl$, prepared by passing a current of dry hydrogen chloride into an ethereal solution of quinoline, melts at 82°.

In Einhorn and Holland's acylation method, whereby the acylation of a given compound is conducted by the action of an acid chloride on its solution in a tertiary base, the assumption that an additive compound is formed from the acid chloride and the tertiary base has been adduced by Einhorn and others. The author describes the additive compounds which acetyl chloride and benzoyl chloride respectively form with quinoline.

The *compound*, $C_9NH_7,AcCl$, prepared by allowing a dry ethereal solution of quinoline and acetyl chloride to remain at a low temperature for a considerable time, forms colourless crystals, is unstable and deliquescent, being readily decomposed into quinoline and acetyl chloride.

The *compound*, $C_9NH_7,BzCl$, prepared in an analogous manner, boils at 105° under 12 mm. pressure, is hygroscopic, and assumes a dark red tint on exposure to air. When acted on by water it forms benzoic anhydride, benzoyl chloride, quinoline, and quinoline hydrochloride.

A. McK.

Kynurine Ethers. Hans Meyer (*Monatsh.*, 1906, **27**, 255—266). Compare this vol., i, 108; Wenzel, Abstr., 1895, i, 70).—The action of sodium methoxide on 4-chloroquinoline in methyl-alcoholic solution at the ordinary temperature for seventeen days, or at 130° for one hour, leads to the formation of 4-*methoxyquinoline*,

$$C_6H_4<\begin{matrix}C(OMe):CH \\ N{=\!=\!=}CH\end{matrix},$$

which solidifies in a freezing mixture, melts at 31°, commences to boil at 245°, and on continued distillation is converted partially into the ψ-methyl ether, the mixture boiling above 360°. The methoxyquinoline is soluble in ether but insoluble in water. The *mercurichloride*, $C_{10}H_9ON,HHgCl_2$, crystallises in long, white needles, melts and decomposes at 188—190°, and is stable towards light; the *platinichloride* forms almost colourless, delicate, glistening scales, and melts and decomposes at 227—228°; the *aurichloride*, $C_{10}H_9ON,HAuCl_4$, forms small, lemon-yellow crystals and melts and decomposes at 196—197°.

When heated at 300—310°, 4-methoxyquinoline is converted completely into the *ψ-methyl ether*,  $C_6H_4<\begin{array}{l}CO—CH\\ NMe\cdot CH\end{array}$, which, when crystallised from water, melts at about 90° and loses water at 110°; the anhydrous substance melts at 143° and is soluble in water or benzene, but is insoluble in ether. When evaporated with hydrochloric acid, it is converted into *kynurine methochloride*, which crystallises in delicate needles and melts at about 178°. The *aurichloride* forms small, light yellow needles and melts at 168—170°; the *platinichloride* crystallises in orange-yellow needles and melts and decomposes at 212°; the crystalline *mercurichloride* melts at 178°.

Wenzel's ethylkynurine (*loc. cit.*) is 4-ethoxyquinoline and not the ψ-ethyl ether, as it yields ethyl iodide, although slowly, when boiled with hydriodic acid of sp. gr. 1·7. When heated at about 360°, it changes into the ψ-ethyl ether,  $C_6H_4<\begin{array}{l}CO—CH\\ NEt\cdot CH\end{array}$, which was isolated as the *aurichloride*. This crystallises in sheaves of lemon-yellow needles and melts and decomposes at 155°. G. Y.

Quinaldinic [Quinoline-2-carboxylic] Acid. EMIL BESTHORN and JOS. IBELE (*Ber.*, 1906, **39**, 2329—2334. Compare Abstr., 1905, i, 612; Meyer, *ibid.*, i, 155, 666).—Quinoline-2-carboxylic acid, prepared by Koenigs' method (Abstr., 1899, i, 389), melts and decomposes at 156°. The authors have repeated the preparation of the chloride and have again obtained the substance melting at 97—98° by using freshly prepared thionyl chloride; if recovered thionyl chloride is employed, the reaction follows another course (compare Meyer, *loc. cit.*). The methyl ester melts at 85° and the amide at 132—133°.

When quinoline-2-carboxylic acid is nitrated at 60—70° with concentrated sulphuric and nitric acids, a mixture of two mononitro-compounds is obtained, which is separated by means of their barium salts. *5-Nitroquinoline-2-carboxylic acid* melts and decomposes at 203°, the 8-*nitro*-compound at 177°. The constitutions are determined by heating them above their melting points, when carbon dioxide is evolved and 5-nitro- and 8-nitro-quinoline respectively are obtained.

C. S.

Nitro- and Amino-derivatives of α-Naphthaquinoline and their Oxidation to Quinoline-7 : 8-dicarboxylic Acid. RUDOLF HAID (*Monatsh.*, 1906, **27**, 315—340).—The two nitro-derivatives of α-naphthaquinoline described by Claus and Imhoff (Abstr., 1898, i, 333) were mixtures. On repeating the nitration under the same conditions and fractionally crystallising the product from alcohol and benzene, the author obtained four nitro-α-naphthaquinolines. Two of these, melting at 175° and 230° respectively, and constituting together 90 per cent. of the product, have the nitro-group in position 7, 8, 9, or 10, as on reduction and oxidation both yield quinoline-7 : 8-dicarboxylic acid.

Nitro-α-naphthaquinoline, $C_{13}H_8N\cdot NO_2$, melting at 230°, crystallises in glistening, yellow needles, or in aggregates of transparent plates which change slowly into the yellow needles. The *hydrochloride* crystallises in white needles and melts at 245—250°; the *nitrate*, $C_{13}H_8O_2N_2,HNO_3$, forms slightly yellow, strongly refracting needles or stout prisms and melts at 220°; the *sulphate* crystallises in glistening needles and melts at 243°. When reduced with stannous chloride and hydrochloric acid, it yields an *amino-a-naphthaquinoline*,

$$C_{13}H_8N\cdot NH_2,$$

which crystallises from alcohol in thin, colourless, transparent, brittle leaflets or rhombic plates and melts at 151°. The *hydrochloride* forms white prisms, commences to decompose at 215°, and dissolves in water, forming a blood-red solution which has an acid reaction.

Nitro-a-naphthaquinoline, $C_{13}H_8O_2N_2$, melting at 175°, crystallises from alcohol in spherical aggregates of long, thin, yellow, glistening needles. The *hydrochloride* crystallises in yellow prisms and melts and decomposes at 220—221°; the *nitrate* forms long needles and melts and decomposes at 193°. When reduced with stannous chloride and hydrochloric acid, the nitro-compound yields an *amino-a-naphthaquinoline*, which crystallises in aggregates of yellow leaflets and melts at 175°; the *hydrochloride* crystallises in long, white, silky needles and commences to decompose at 230°.

Nitro-a-naphthaquinoline, melting at 166°, crystallises from alcohol in white needles or leaflets. The *hydrochloride* forms long, delicate, white needles and loses hydrogen chloride above 100°; the *nitrate* forms yellow needles, commences to decompose at 125°, and is melted at 150°.

Nitro-a-naphthaquinoline, melting at 155°, crystallises in long, yellow, glistening needles and is readily soluble in alcohol or benzene. The *hydrochloride* forms yellow, strongly refracting needles and melts and decomposes at 210—211°; the *nitrate* forms yellow, strongly refracting needles and melts at 178°.

Quinoline-7 : 8-dicarboxylic acid, $C_{11}H_7O_4N,H_2O$, prepared by the oxidation of the above amino-a-naphthaquinolines with dilute potassium permanganate in dilute sulphuric acid solution cooled by ice, crystallises in stellate aggregates of microscopic prisms, melts and decomposes at 206—207°, and yields an odour of quinoline when sublimed. The *hydrochloride* crystallises in long prisms and melts and decomposes at 212°; the *sodium hydrogen* ($+3H_2O$), *acid copper*, *normal copper* ($+\frac{1}{2}H_2O$), *nickel*, *lead*, and *silver* salts are described.

The amine melting at 175° yields on oxidation, together with quinoline-7 : 8-dicarboxylic acid, an amorphous product which is probably a-phenylpyridinedicarboxylic acid. G. Y.

Quinonaphthalone. ALEXANDER EIBNER and M. LÖBERING (*Ber.*, 1906, 39, 2215—2218. Compare Eibner, Abstr., 1904, i, 1049).—*s*-Quinonaphthalone, $C_{22}H_{13}O_2N$, prepared by heating 1 : 8-naphthalic anhydride with 2-methylquinoline and zinc chloride at 210°, forms long, matted, greenish-yellow needles, melts at 261°, is readily soluble in chloroform or glacial acetic acid, and forms traces of an unstable, dark red compound with aniline. The *sodium* derivative, $C_{22}H_{12}O_2NNa$, crystallises from alcohol in sheaves of yellowish-red needles and is decomposed by dilute mineral acids or much water. The action of bromine on quinonaphthalone in chloroform solution at 50—60° leads to the formation of a *perbromide*, $C_{22}H_{12}O_2NBr_4$, which crystallises in small, glistening, orange-yellow leaflets, melts and loses bromine at 239°, decomposes when recrystallised from chloroform, and yields quinonaphthalone when treated with alcohol, water, or ammonia. The *perbromide*, $C_{22}H_{12}O_2NBr_6$, formed by the action of an excess of bromine on quinonaphthalone in cold chloroform solution, crystallises in long, matted, yellowish-brown needles, and when heated with water yields a *monobromo*-derivative, which crystallises in white leaflets, becomes yellow, and yields quinonaphthalone when recrystallised (compare Eibner and Merkel, Abstr., 1902, i, 494).

as-*Quinonaphthaline*, $C_{22}H_{14}ON_2$, prepared by heating naphthalimide with 2-methylquinoline and zinc chloride at 180°, crystallises in long, orange-red needles, melts at 235°, is only sparingly soluble in alcohol, ether, or light petroleum, and with bromine in chloroform solution forms a *bromo*-derivative, which crystallises in light brown needles and forms a blood-red precipitate with diazonium chloride in sodium hydroxide solution.

as-Quinonaphthalone, *as*-quinophthaline, and *as*-quinonaphthaline decolorise potassium permanganate rapidly in cold acetone solution, whereas *s*-quinophthalone and *s*-quinonaphthalone give a red coloration with potassium permanganate, which is decolorised only on prolonged heating. The action of the *s*- as also of the *as*-compounds on potassium permanganate is accelerated by the presence of sodium carbonate. G. Y.

Influence of Nuclear Substituents on the Shade of Malachite-green. Emilio Noelting and Paul Gerlinger (*Ber.*, 1906, **39**, 2041—2053).—E. and O. Fischer have already shown that a nitro-substituent in the para-position produces a yellower shade of green, but in the ortho-position a bluer shade, and that it is practically without effect in the meta-position. Similar generalisations hold good with respect to methyl, chlorine, and methoxyl, chlorine producing the greatest effect and methoxyl the least. p′p″-*Tetramethyldiamino*-o‴-*methyltriphenylmethane*, $C_6H_3Me{\cdot}CH(C_6H_3{\cdot}NMe_2)_2$, is most readily prepared (95 per cent. yield) by condensing *o*-tolualdehyde with dimethylaniline, and may also be obtained, although not in a crystalline form, by eliminating the amino-group from the condensation product of Michler's hydrol and *m*-toluidine, or by the action of phosphorus oxychloride on *o*-toluic acid and dimethylaniline. It crystallises from alcohol in glistening needles, melts at 102—103°, and when oxidised with lead peroxide and hydrochloric acid yields a dye, the *additive* compound of which, with zinc chloride, forms green crystals with a bronze lustre and yields blue solutions. The sulphonic acid of the leuco-compound yields a *barium* salt, $(C_{24}H_{27}O_3N_2S)_2Ba,8H_2O$, in the form of soft, glistening plates, which readily turn green on exposure to the air.

The corresponding p′p″-*tetramethyldiamino*-m‴-*methyltriphenylmethane*, obtained from *m*-tolualdehyde, crystallises from alcohol in colourless needles and melts at 84—85°. When oxidised, it yields a copper-red dye, but the aqueous solutions are bluish-green and so impart a blue colour to fabrics. The *p*‴-methyl derivative (Hanzlik and Bianchi, Abstr., 1899, i, 597) yields an oxidation product which dyes yellowish-green. The leuco-compound yields a *sulphonic acid*, the *sodium* salt of which, $C_{24}H_{27}N_2{\cdot}SO_3Na,2\frac{1}{2}H_2O$, when oxidised yields a dye which imparts the same colour to a fabric as the non-sulphonated dye. The 2 : 3 : 6-trimethyl derivative, $C_6H_2Me_3{\cdot}CH(C_6H_4{\cdot}NMe_2)_2$, prepared by eliminating the amino-group from aminotetramethyldiaminotrimethyltriphenylmethane (Abstr., 1892, 187), has not been obtained in a crystalline form. When oxidised it yields a dark red dye which dissolves in water to a blue solution. o'''-Chloro-$p'p''$-tetramethyldiaminotriphenylmethane crystallises from alcohol or toluene in glistening needles, melts at 145—146°, and on oxidation yields Geigy's setocyanin. The zincochloride dyes a greenish-blue. The *sulphonic acid* of the leuco-compound yields a *calcium* salt,

$$(C_{23}H_{24}N_2Cl{\cdot}SO_3)_2Ca,11H_2O,$$

which crystallises from water in glistening needles. When oxidised it yields a product which dyes blue.

The m'''-*chloro*-derivative, when crystallised from alcohol mixed with a little zinc dust, forms colourless needles, melts at 112°, and dissolves readily in most organic solvents. The p'''-chloro-derivative melts at 98—99°, and not at 142—143° as stated by Kaeswurm (Abstr., 1886, 552).

p'p''-*Tetramethyldiamino*-o'''-*methoxytriphenylmethane*, obtained by condensing dimethylaniline and the methyl ether of salicylaldehyde with alcoholic hydrochloric acid, crystallises from alcohol in glistening needles, melts at 146°, and is only sparingly soluble in ether. The *sodium* salt of the *sulphonic acid* crystallises in glistening plates, and the *ammonium* salt, $C_{24}H_{27}ON_2{\cdot}SO_3NH_4,H_2O$, in slender needles. The m'''-*methoxyleucomalachite-green* forms glistening plates melting at 123° and is fairly readily soluble in alcohol or ether. The isomeric p'''-*methoxy*-compound melts at 105° and dissolves readily in most organic solvents. The *barium* salt of the *sulphonic acid*,

$$(C_{24}H_{27}ON_2{\cdot}SO_3)_2Ba,7H_2O,$$

and the *sodium* salt, $C_{24}H_{27}ON_2{\cdot}SO_3Na,8H_2O$, have been analysed.

A small amount of p'p''-*tetramehyldiaminotriphenylmethane*-3'''-*sulphonic acid* has been obtained by oxidising the corresponding sulphinic acid, prepared by the action of sulphur dioxide and copper powder on diazotised m'''-aminoleucomalachite-green. When oxidised it yields a green dye similar to malachite-green. J. J. S.

Derivatives of 3-Hydroxy-1-phenyl-5-pyrazolone. MAX CONRAD and A. ZART (*Ber.*, 1906, 39, 2282—2288. Compare Michaelis and Burmeister, Abstr., 1892, 1004; 1899, i, 233).—3-Hydroxy-1-phenyl-5-pyrazolone can be prepared directly, in 64 per cent. yield from sodium, ethyl malonate, and phenylhydrazine in alcoholic solution; after removal of the alcohol, the residue is heated at 110—120° for twelve hours, cooled, dissolved in water, and, after extraction with ether, the aqueous portion is acidified and the precipitate recrystallised.

4-*Amino-3-hydroxy*-1-*phenyl-5-pyrazolone*, obtained by reducing the nitroso-compound (Michaelis, *loc. cit.*) with ammonium sulphide at 30—40°, is a yellow substance which decomposes at 320° and is insoluble in acids.

3-*Hydroxy*-1-*phenyl*-4 : 4-*diethyl*-5-*pyrazolone*, obtained as above from ethyl diethylmalonate, crystallises in long, prismatic needles, melts at 114—115°, and can be heated in alkaline solution for a long time without decomposition.

3-*Methoxy*-1-*phenyl*-4 : 4-*diethyl*-5-*pyrazolone*, obtained from an alkaline solution of the preceding compound and methyl sulphate, forms pearly leaflets, melts at 94—95°, and is soluble after long boiling in aqueous solutions of alkali hydroxides, from which sulphuric acid precipitates the unchanged substance in crystals containing $2H_2O$ and melting completely at 166°. Of the $2H_2O$, 1 mol. is water of crystallisation, the other of constitution. Sodium hydroxide neither hydrolyses the compound nor breaks the ring (compare Michaelis (*loc. cit.*).

3-*Acetoxy*-1-*phenyl*-4 : 4-*diethyl*-5-*pyrazolone* melts at 97°, and the corresponding *benzoyl* derivative at 110°.

3-*Hydroxy*-1-*phenyl*-4 : 4-*dipropyl*-5-*pyrazolone*, obtained in similar manner to the diethyl compound, forms short prisms and melts at 103—105°; *dipropylmalonic acid phenylhydrazide*,

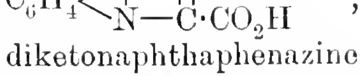
$$CO_2H\cdot CPr_2\cdot CO\cdot NH\cdot NHPh,$$

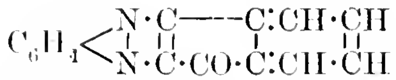
which occurs as a by-product, melts at 148° evolving carbon dioxide.

3-*Hydroxy*-1-*phenyl*-5-*pyrazolonimide*,  $\begin{array}{l}N\cdot NPh\\ \|\\ OH\cdot C\cdot CH_2\end{array}\!\!>C{:}NH$, obtained from sodium ethoxide, phenylhydrazine, and ethyl cyanoacetate, crystallises in prisms, melts at 219°, and is soluble in mineral acids or in alkalis. By treatment with sodium nitrite and dilute acetic acid, a quantitative yield of the iso*nitroso*-compound is obtained, which melts and decomposes at 223°.

3-*Hydroxy*-1-*phenyl*-4 : 4-*diethyl*-5-*pyrazolonimide*, obtained from ethyl cyanodiethylacetate, separates from hot water in crystals containing $2H_2O$, melts at 211—213°, and is not changed by boiling dilute mineral acids.
C. S.

Oxidation of Naphthaphenazine by Chromic Acid. II. OTTO FISCHER and ERICH SCHINDLER (*Ber.*, 1906, 39, 2238—2244. Compare Abstr., 1904, i, 111).—A convenient method of preparing diketonaphthaphenazine by the oxidation of naphthaphenazine by chromic acid is described.

Hydroxyphenylquinoxalinecarboxylic acid,  $C_6H_4\!<\!\begin{array}{l}N—C\cdot C_6H_4\cdot OH\\ \;|\qquad \|\\ N—C\cdot CO_2H\end{array}$, is one of the products obtained by boiling diketonaphthaphenazine with a concentrated aqueous solution of sodium hydroxide; crystallises in silvery, flat prisms or leaflets, is easily soluble in hot water, and melts at 237°, water being eliminated and the stable lactone formed. Its solution in concentrated sulphuric acid is yellow. Its *barium* salt forms silky needles. Its *lactone*, $C_{15}H_8O_2N_2$, formed by heating the acid either alone or with glacial acetic acid or acetic anhydride, exhibits dimorphism, separating from benzene or acetone in prisms, which are gradually transformed into hexagonal crystals; it melts at 207—208°.

The lactone may also be formed directly from diketonaphthaphenazine by oxidising it, under the conditions described, with chromic acid. *Ketoindenephenazine*,  $C_6H_4<\begin{matrix}N\cdot C\text{——}C:CH\cdot CH\\ N\cdot C\cdot CO\cdot C:CH\cdot CH\end{matrix}$, formed as a by-product in the preceding reaction, separates from glacial acetic acid in yellow prisms and melts at 187°. It forms a brownish-red solution with concentrated sulphuric acid. Its *phenylhydrazone* separates from alcohol in red needles and melts at 216—217°.

Phenylquinoxalinecarboxylic acid,  $C_6H_4<\begin{matrix}N\cdot C\cdot C_6H_4\cdot CO_2H\\ N\cdot CH\end{matrix}$, obtained by fusing diketonaphthaphenazine with sodium hydroxide until vapours are evolved, differs from hydroxyphenylquinoxalinecarboxylic acid in being sparingly soluble in water. It melts and decomposes at about 275°, and forms a yellow solution with concentrated sulphuric acid. It is a weak acid. When distilled, it loses carbon dioxide and is transformed into phenylquinoxaline. A. McK.

o-Hydroxytriphenylmethane Derivatives. EMILIO NOELTING and PAUL GERLINGER (*Ber.*, 1906, **39**, 2053—2056).

—p′p″p‴-*Hexamethyltriamino*-o‴-*hydroxytriphenylmethane*,

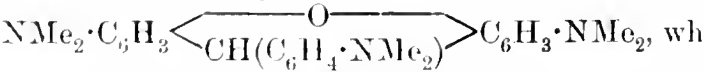
$$NMe_2\cdot C_6H_3(OH)\cdot CH(C_6H_4\cdot NMe_2)_2,$$

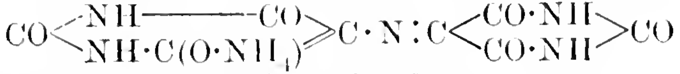
obtained by condensing dimethyl-*m*-aminophenol with Michler's hydrol in an alcoholic solution of hydrogen chloride, crystallises from alcohol in colourless needles and melts and decomposes at 172—174°. It turns red in contact with the air and dissolves readily in most organic solvents, but is not readily oxidised to a dye owing to the presence of the *o*-hydroxy-group. The *acetyl* derivative, $C_{25}H_{30}ON_3Ac$, crystallises from alcohol mixed with a small amount of zinc dust in colourless needles melting at 171—173°. It changes colour more readily than the original hydroxy-compound on exposure to the air, and is readily oxidised by lead peroxide to the corresponding dye; the *additive* compound of the chloride with zinc chloride forms a dark violet powder which dyes fabrics purple-blue. The *picrate* is sparingly soluble.

p′p″p‴-*Hexamethyltriamino*-o′o″-*dihydroxytriphenylmethane*,

$$NMe_2\cdot C_6H_4\cdot CH[C_6H_3(OH)\cdot NMe_2]_2,$$

obtained by condensing dimethyl-*m*-aminophenol with dimethyl-*p*-aminobenzaldehyde in alcoholic hydrogen chloride, crystallises from dilute alcohol in colourless needles melting and decomposing at 175°. It gradually turns red on exposure to the air, and dissolves readily in organic solvents and in alkalis. The hydroxylic compound is not readily oxidised, but with acetic acid and lead peroxide yields a bluish-red dichroic solution which gives a violet-blue colour when diluted. The *diacetyl* derivative, $C_{25}H_{29}O_2N_3Ac_2$, forms a pale red mass which does not crystallise. On exposure to the air, it gradually turns blue, and can be oxidised readily to a dye, the chloride of which forms a violet powder with zinc chloride.

When the dihydroxy-derivative is warmed with concentrated sulphuric acid on the water-bath, it yields the non-crystalline *anhydroleuco-compound*,  $NMe_2\cdot C_6H_3<\begin{matrix}\text{——}O\text{——}\\ CH(C_6H_4\cdot NMe_2)\end{matrix}>C_6H_3\cdot NMe_2$, which is readily oxidised to a dye when heated at 140° with concentrated sulphuric acid. The dye base is dark red and the salts dark green, but produce a violet colour on the fabric. Solutions in mineral acids have an intense reddish-yellow colour and are strongly fluorescent. The compound is a dimethyl-*p*-amino-derivative of rosamine. J. J. S.

Constitution of Murexide and of Purpuric Acid. RICHARD MÖHLAU and HANS LITTER (*J. pr. Chem.*, 1906, [ii], **73**, 449—472. Compare Möhlau, Abstr., 1904, i, 654; Slimmer and Stieglitz, Abstr., 1904, i, 634; Piloty and Finckh, *ibid.*, 820).—The authors consider that the formulæ  $CO<\begin{matrix}NH\text{——}CO\\NH\cdot C(OH)\end{matrix}>C\cdot N:C<\begin{matrix}CO\cdot NH\\CO\cdot NH\end{matrix}>CO$ for purpuric acid and  $CO<\begin{matrix}NH\text{———}CO\\NH\cdot C(O\cdot NH_4)\end{matrix}>C\cdot N:C<\begin{matrix}CO\cdot NH\\CO\cdot NH\end{matrix}>CO$ for murexide are in accordance with the following facts:

The action of alloxan on ethyluramil in presence of ammonium carbonate leads to the formation of murexide and alcohol.

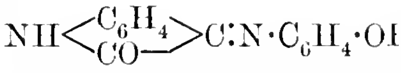
Alkylpurpuric acids cannot be prepared by oxidation of dibarbiturylalkylamines. Alkylamine purpurates are formed by the action of alkylamines on alloxan and alloxantin, or of alkylamine carbonates and acetates on alloxan. The reddish-orange purpuric acid is unstable towards water. The formation of an unstable methyl purpurate by the action of methyl iodide on silver purpurate (Slimmer and Stieglitz, *loc. cit.*) is confirmed.

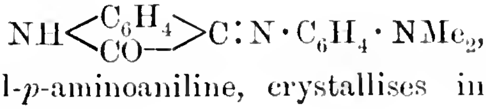
The relation of the constitution of murexide to its dyeing properties is discussed.

The hydrolysis of murexide by boiling water, or by cold or boiling dilute hydrochloric acid, leads to the formation on the one hand of uramil and alloxan, and on the other of alloxantin. As these products are further hydrolysed by prolonged boiling with water, their amounts are at any time a function of the duration of the hydrolysis.

Methylamine purpurate, $C_9H_{10}O_6N_6,H_2O$, forms red, microscopic, rhombic crystals, or large, green, shimmering rhomboids, loses H_2O at 110°, decomposes at 210°, and when heated with water yields 7-methyluramil, alloxantin, alloxan, and methylamine.

Ethylamine purpurate, $C_{10}H_{12}O_6N_6,H_2O$, forms red prisms, decomposes about 205°, and when heated with water yields alloxan, ethylamine, traces of alloxantin, and *7-ethyluramil*, $C_6H_9O_3N_3$, which crystallises in hexagonal prisms.

p-*Hydroxyphenylimesatine*,  $NH<\begin{matrix}C_6H_4\\CO\end{matrix}>C:N\cdot C_6H_4\cdot OH$, prepared by boiling isatin with *p*-aminophenol hydrochloride in alcoholic solution in presence of sodium acetate, crystallises in red prisms, melts above 300°, is insoluble in water or benzene, but is sparingly soluble in toluene, chloroform, methyl alcohol, or ethyl acetate, and is readily so in pyridine; it dissolves in aqueous alkali hydroxides forming a red, in concentrated sulphuric acid forming a reddish-brown, solution, and is hydrolysed by boiling dilute acids, forming isatin and *p*-aminophenol.

p-*Dimethylaminophenylimesatine*,  $NH<\begin{matrix}C_6H_4\\CO\end{matrix}>C:N\cdot C_6H_4\cdot NMe_2$, prepared from isatin and dimethyl-*p*-aminoaniline, crystallises in glistening, metallic leaflets and melts at 215°.

p-*Aminophenylimesatine*, $NH<\substack{C_6H_4\\CO}>C:N\cdot C_6H_4\cdot NH_2$, crystallises in reddish-brown needles and melts above 300°. G. Y.

Action of Primary Amines on Alloxantin. RICHARD MÖHLAU and HANS LITTER (*J. pr. Chem.*, 1906, [ii], **73**, 472—487. Compare Möhlau, Abstr., 1904, i, 654).—Dibarbiturylalkylamines, prepared together with alloxan by boiling alloxantin, or alone by boiling dialuric acid with the hydrochlorides of primary amines in aqueous solution (Möhlau, *loc. cit.*), are colourless, crystalline, dibasic acids, dissolve in dilute alkali carbonates or hydroxides, and are hydrolysed by boiling aqueous alkali hydroxides, forming dialuric acid and the amine.

Dibarbiturylmethylamine (*loc. cit.*), which is formed also by the action of dialuric acid on 7-methyluramil, decomposes at 280° and reddens blue litmus solution. The *sodium* salt, $C_9H_7O_6N_5Na_2$, crystallises from alcohol.

Dibarbiturylethylamine, $NEt(C_4H_3O_3N_2)_2$, forms rhombic crystals, becomes red at 235°, but is not completely decomposed at 300°, and in aqueous solution has an acid reaction. The *sodium* salt, $C_{10}H_9O_6N_5Na_2$, crystallises in needles.

Dibarbiturylphenylamine, $NPh(C_4H_3O_3N_2)_2$, crystallises in white needles, becomes blue at 240°, and is oxidised superficially, becoming green on exposure to air.

Dibarbituryl-α-naphthylamine, $C_{10}H_7\cdot N(C_4H_3O_3N_2)_2$, becomes black at 260° and forms a *sodium* salt, $C_{18}H_{11}O_6N_5Na_2$, which crystallises in glistening leaflets.

Dibarbituryl-β-naphthylamine crystallises in colourless needles, decomposes at 260°, and is insoluble in indifferent solvents. The *sodium* salt, $C_{18}H_{11}O_6N_5Na_2$, crystallises in large leaflets.

The action of benzylamine on alloxantin leads to the formation of *benzyluramil*, $CH_2Ph\cdot NH\cdot C_4H_3O_3N_2$, which crystallises from hot glacial acetic acid in needles, decomposes at about 280°, and has feeble basic properties, crystallising from its solution in concentrated hydrochloric acid on cooling, but forms a *sodium* salt, $C_{11}H_9O_3N_3Na_2$; this crystallises in tetragonal prisms. When heated with aqueous sodium hydroxide, the uramil is slowly hydrolysed, forming benzylamine.

Phenylethyluramil, $CH_2Ph\cdot CH_2\cdot NH\cdot C_6H_3O_3N_2$, formed by the action of β-phenylethylamine on alloxantin, crystallises in prisms, melts above 300°, is readily soluble in aqueous sodium carbonate, has feeble basic properties, and is hydrolysed by boiling sodium hydroxide, forming phenylethylamine and dialuric acid.

Dibarbiturylcarbamide, $CO(NH\cdot C_4H_2O_3N_2)_2$, is formed by boiling alloxantin with carbamide and hydrochloric acid in aqueous solution in a reflux apparatus; it crystallises in spears, decomposes above 300°, and is readily soluble in aqueous sodium carbonate or alkali hydroxides, forming solutions which evolve ammonia when boiled.

Alloxazine (Kühling, Abstr., 1891, 1341), prepared from alloxantin and *o*-phenylenediamine hydrochloride, forms a greyish-green powder and decomposes above 300°. The *sodium* salt, $C_{10}H_4O_2N_4Na_2$, crystallises in yellow needles.

Alloxantin and *m*-phenylenediamine hydrochloride interact, forming a dark brown to black, amorphous *precipitate.*

Bisanhydroalloxan-p-*phenylenediamine,* $C_6H_4(N:C_4H_3O_3N_2)_2$, prepared from alloxantin and *p*-phenylenediamine hydrochloride, forms blue needles with green lustre, melts above 300 , and dissolves in concentrated sulphuric acid or aqueous alkali hydroxides or carbonates, forming a bluish-violet solution. When boiled with an aqueous alkali hydroxide, it is hydrolysed to the diamine and alloxan, the solution becoming colourless, but as the solution cools the anhydro-compound is re-formed.

Dibarbituryl-p-*phenylenediamine.* $C_{14}H_{12}O_6N_6$, is formed by the action of dialuric acid on *p*-phenylenediamine hydrochloride; it crystallises in colourless prisms, is readily soluble in aqueous sodium carbonate or hydroxide, and when boiled with alloxan in aqueous solution is oxidised slowly, in ammoniacal solution more rapidly, yielding bisanhydro-alloxan-*p*-phenylenediamine.

Dibarbituryl-2 : 5-tolylenediamine, $C_6H_3Me(NH\cdot C_4H_3O_3N_2)_2$, prepared from alloxantin and tolylene-2 : 5-diamine hydrochloride, forms colourless crystals, melts above 300°, is readily soluble in aqueous sodium hydroxide or carbonate or concentrated hydrochloric acid, and when oxidised with potassium permanganate in hot dilute sulphuric acid solution yields a blue, flocculent *product* (*bisanhydroalloxan-2 : 5-tolylenediamine ?*).

Dibarbiturylbenzidine, $C_{12}H_8(NH\cdot C_4H_3O_3N_2)_2$, prepared from alloxantin and benzidine hydrochloride, is obtained as a greyish-white, amorphous, flocculent substance, and is not hydrolysed by boiling aqueous sodium hydroxide; the *sodium* salt, $C_{20}H_{14}O_6N_6Na_2$, crystallises in colourless needles. G. Y.

Mixed Azo-compounds. II. ALEXANDER EIBNER and O. LAUE (*Ber.*, 1906, **39**, 2022—2027).—1-Phenyl-3-methylpyrazoloneazobenzene (Abstr., 1903, i, 871) reacts with a chloroform solution of bromine, yielding dark reddish-brown crystals of the perbromide, $C_{16}H_{12}ON_4Br_6$, which with ammonia yields *dibromophenylmethylpyrazoloneazobenzene,* $C_{16}H_{12}ON_4Br_2$. This crystallises from a mixture of ether and chloroform in slender, orange-red needles and melts at 227°.

With sodium hydroxide or, better, sodium ethoxide, it yields a crystalline *sodium* derivative, $C_{16}H_{11}ON_4Br_2Na$, and when reduced with tin and hydrochloric acid it yields dibromorubazonic acid, melting at above 300°, and *p*-bromoaniline. It has not been found possible to couple mono-substituted pyrazolone derivatives which contain the substituent in the methylene group with diazobenzene.

Phenylhydrazineketopyrazolonecarboxylic acid does not yield a perbromide, but simply a mono-substituted derivative, $C_{10}H_{11}O_3N_4Br$, which crystallises from glacial acetic acid in golden-yellow needles and melts at 258°.

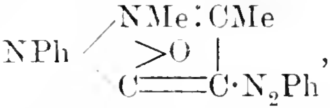
Phenylhydrazineketopyrazolone dissolves in sodium hydroxide solution, and with a chloroform solution of bromine yields a *perbromide*, $C_{1}.H_{11}ON_4Br_3$. This crystallises in dark reddish-brown prisms and reacts with alkali, yielding compact crystals of a *bromo*-derivative,

$C_{15}H_{11}ON_4Br$, melting at 224°. When reduced with zinc dust and acetic acid, the carboxylic acid yields aniline and rubazonecarboxylic acid (Bernthsen, *Chem. Zeit.*, 1898, 457). The monobromo-derivative yields *p*-bromoaniline and rubazonecarboxylic acid.

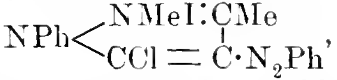
These reactions indicate that the acid is an azo-compound, namely, the carboxylic acid of ketophenylpyrazoloneazobenzene. The views of Bernthsen and R. Meyer regarding the structure of tartrazin are thus confirmed.

Ketophenylpyrazoloneazocarboxylic acid yields a *disodium* derivative, $C_{16}H_{10}O_3N_4Na_2$, in the form of golden-yellow crystals which are readily hydrolysed by water to the monosodium salt. *cyclo*Pentadieneazobenzene also forms a *perbromide*. J. J. S.

Benzeneazo-derivatives of Antipyrine and Thiopyrine.

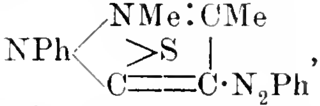
August Michaelis and H. Schlecht (*Ber.*, 1906, **39**, 1954—1956).—4-*Benzeneazoantipyrine*,  $NPh\langle\begin{matrix}NMe{:}CMe\\ >O\ |\\ C{=\!=}C\cdot N_2Ph\end{matrix}$, is formed by heating 4-benzeneazo-1-phenyl-3-methyl-5-pyrazolone with methyl sulphate; it crystallises in reddish-yellow leaflets, melts at 174°, is readily soluble in alcohol or in hydrochloric acid, forming a deep red solution, and is insoluble in aqueous sodium hydroxide.

4-*Benzeneazo-5-chloro-1-phenyl-3-methylpyrazole methiodide*,



$$NPh{<}\begin{matrix}NMeI{:}CMe\\ CCl=C\cdot N_2Ph\end{matrix},$$

is prepared by treating 4-benzeneazo-5-chloro-1-phenyl-3-methylpyrazole (Michaelis and Leonhardt, Abstr., 1904, i, 124) with an excess of methyl sulphate, neutralising the product with sodium carbonate, and adding a concentrated solution of potassium iodide; it crystallises in slender, yellow needles and melts at 170°. The *methochloride*, prepared by boiling the methiodide with silver chloride in aqueous-alcoholic solution, forms reddish-yellow crystals and melts at 164°.

When treated with potassium hydrogen sulphide in aqueous solution, the methiodide yields 4-*benzeneazothiopyrine*,  $NPh\langle\begin{matrix}NMe{:}CMe\\ >S\ |\\ C{=\!=}C\cdot N_2Ph\end{matrix}$, which forms stout, dark red crystals, melts at 216°, is readily soluble in alcohol, and with acids forms unstable, dark red salts (compare Michaelis, Leonhardt, and Wahle, Abstr., 1905, i, 392). G. Y.

The Rendering Insoluble of Gelatin during Photographic Development, particularly by the Use of Pyrogallol Developers.

Auguste Lumière, Louis Lumière, and Alphonse Seyewetz (*Bull. Soc. chim.*, 1906, [iii], **35**, 377—381. Compare Abstr., 1905, i, 847, 848).—The results of experiments with a number of developers show that gelatin only becomes insoluble when the developers are in presence of alkali and in contact with air, and that probably the active agents in rendering the gelatin insoluble are the oxidation products formed from the developers. Where the oxidation product is insoluble in dilute alkalis, as in the case of *p*-aminophenol, the action is slight. The action is usually most marked in the neighbourhood of the reduced silver, and this is probably due to the more rapid oxidation of the developer in that region by the bromine liberated. T. A. H.

Action of Ozone and other Oxidising Agents on Lipase. JOSEPH H. KASTLE (*Chem. Centr.*, 1906, i, 1555—1556; from *Public Health and Marine-Hospital Service of the U.S. Hygienic Lab. Bull.* No. 26, 37—41).—The activity of a quantity of lipase from pig's liver which was found capable of hydrolysing 0·058 gram of ethyl butyrate in four and a quarter hours was destroyed by the action of 1·009 mg. of ozone in forty minutes. When a second quantity of lipase, which under normal conditions hydrolysed 0·058 gram of ethyl butyrate in twenty-four hours, was treated with 0·312 mg. of ozone, its hydrolytic action sank to 0·00116 gram in twenty-four hours.

Silver nitrate, hydriodic acid, formaldehyde, cresols, hydrocyanic acid, potassium nitrate, and succinic acid had practically no poisonous action on lipase; mercuric chloride, chromic acid, copper sulphate, and perosmic acid were moderately poisonous; ozone, chlorine, bromine, sodium fluoride, cyanogen iodide, and potassium permanganate were strongly poisonous. The poisonous effect of cyanogen iodide increased with rise of temperature. E. W. W.

Stability of Oxydases and their Behaviour towards Various Reagents. JOSEPH H. KASTLE (*Chem. Centr.*, 1906, i, 1554—1555; from *Public Health and Marine-Hospital Service of the U.S. Hygienic Lab. Bull.* No. 26, 7—22).—The oxydase of *Sepiota americana* retains its activity for weeks or months and appears to be more stable in glycerol than in water. The presence of oxydases has been detected in the aqueous and glycerol extracts of a number of moulds indigenous to Columbia, but not in the extracts of the very poisonous *Amanita verna*. Whilst the oxidising action of the glycerol extracts of *Lactarius piperatus, Lactarius volumen,* and *Lactarius indigo* did not decrease in four months, in other cases, for instance, in that of *Volvaria bombycina*, the activity of the extract rapidly diminished. The oxydases are less stable in water than in glycerol and are not so rapidly destroyed by toluene as by chloroform or thymol. The oxydases of *Lepiota americana* are precipitated from the aqueous solution by alcohol in a colloidal form. An aqueous solution of material which had been dried in the air and exposed for four and a half months gave a strong blue coloration with guaiacum tincture. The oxidising power of the substance is destroyed at 80—90°, but it withstands heating for a short time at 80°. When the fresh mould is kept for some time in an atmosphere of hydrogen, reducing substances are formed which decolorise guaiacum-blue; the formation of these compounds may be due to anaërobic bacteria or to the mould itself. The oxydase is more readily soluble in water than in other solvents, and is not destroyed by a 40 per cent. solution of formaldehyde; it is insoluble in ethyl or amyl alcohol and its activity is not affected. It dissolves in glycerol and apparently to a certain extent in toluene. Certain substances such as chlorine hydrate completely destroy the oxydase.

A deep purple-red coloration is produced when aqueous potato extract is added to a slightly alkaline solution of leucorosolic acid, but strongly alkaline or acid solutions are scarcely oxidised. The ethyl ester of phenolphthalein gives a similar reaction, but the presence of bromine in the ethyl ester of tetrabromophenolphthalein appears to prevent oxidation by vegetable oxydases; benzoyl peroxide and benzoyl acetyl peroxide oxidise the latter compound, however, forming a bluish-green coloration. An alcoholic solution of aloin gives a red coloration with vegetable oxydases; the sensitiveness of the reagent is considerably increased by shaking with zinc dust, filtering, and exposing to air for a short time, but it loses its property in some days. The red substance which is formed is soluble in water and in the aqueous extracts containing oxydases: it is more stable than the blue compound formed by the oxidation of guaiacum tincture. The sensitiveness of the aloin and guaiacum reactions is about the same. The intensity of the peroxydase reaction of aloin in aqueous extracts of the leaves of *Phytolacca decandra* depends on the concentration of the hydrogen peroxide, but if only small quantities are used there is but little variation. Whilst the peroxydase reaction of extracts of horseradish, potato parings, and other vegetable oxydases is improved by the addition of a small quantity of hydrogen peroxide, larger quantities are required in the case of animal oxydases. E. W. W.

Peroxydases as Specifically-acting Enzymes. ALEXIS BACH (*Ber.*, 1906, **39**, 2126—2129).—Tyrosine is not oxidised by the system peroxydase—hydrogen peroxide, although the oxidation reactions of ordinary oxydases are effected by this system. The specific action of tyrosinase in oxidising tyrosine is to be ascribed either to the specific nature of its peroxydases or of its oxygenases (since all oxydases are mixtures of peroxydases and oxygenases); the author has accordingly separated, with partial success, the peroxydases of tyrosinase from the oxygenases. Potato juice was used; the fresh juice oxidised tyrosine rapidly, whilst after the treatment with alcohol described, the oxygenases were almost entirely destroyed; the final product contained peroxydases, but had very little oxidising action on tyrosine. On the supposition that the falling off of the tyrosine action was due to the partial destruction of the oxygenases, the latter were replaced by hydrogen peroxide, the addition of which caused the solution to exert an oxidising action on tyrosine.

Similar results were obtained with the mixture of ordinary oxydases and of tyrosinase contained in the juice of *Lactarius velereus.* The specific action of tyrosinase is due to the specific nature of its peroxydases.

Various theoretical considerations are adduced. A. McK.

Organic Chemistry.

Purification of Acetylene by means of Calcium Hypochlorite. Hugo Ditz (D.R.-P. 162324).—In the purification of acetylene by means of commercial bleaching powder, spontaneous heating occurs, and explosions may arise from the formation of chlorine and nitrogen chloride. This is avoided by using the definite compound $CaO,CaOCl_2,2H_2O$ or the compound $CaO,CaOCl_2,H_2O$, obtained by heating the former (Abstr., 1901, ii, 239). These substances do not evolve chlorine when heated, but decompose at 130—140°, evolving oxygen.
C. H. D.

aci-Esters of Nitroform. Arthur Hantzsch and K. S. Caldwell (*Ber.*, 1906, **39**, 2472—2478).—*aci*-Methylnitroform has not been obtained, but in the reaction between methyl iodide and silver nitroform a small amount of nitroform is always obtained, the quantity increasing with diminishing temperature; its production is due to the hydrolysis of the *aci*-methyl ester by the water from the hydrated silver nitroform.

Ethereal solutions of hydrated silver nitroform and of methyl iodide react at $-75°$ with the instantaneous separation of an intensely yellow substance, aci-*silver nitroform di-methyl iodide,* $C(NO_2)_2{:}NO{\cdot}OAg,2MeI$, which from the rapidity of its formation is regarded as an additive compound and not as having the constitution $C(NO_2)_2{:}NO{\cdot}OMe,AgI,MeI$. The substance is very unstable and decomposes spontaneously at 6—8° in air or in indifferent anhydrous solvents into silver iodide and trinitroethane, but in the presence of water nitroform is produced quantitatively.

The theoretical importance of these decompositions is discussed.

Benzyl iodide and allyl iodide yield similar additive compounds which are even less stable. Ethyl iodide, which at the ordinary temperature yields trinitropropane, an oil with the odour of nitrous acid, does not react at low temperatures with silver nitroform.
C. S.

Trinitromethane and Triphenylmethane. Arthur Hantzsch (*Ber.*, 1906, **39**, 2478—2486).—[With K. S. Caldwell.]—*Iodopicrin*, $CI(NO_2)_3$, obtained from iodine and silver nitroform, melts and turns brown at 58°, is decomposed by silver nitrate, slowly in the cold, more rapidly on boiling, reacts with potassium hydroxide in accordance with the equation $3CI(NO_2)_3 + 6KOH = 3C(NO_2)_3K + 2KI + KIO_3 + 3H_2O$, and with silver nitrite yields tetranitromethane. Hexanitroethane is not obtained in the preceding preparation, or by treatment of iodopicrin with silver nitroform, and the author uses this fact as an argument for regarding Gomberg's triphenylmethyl as hexaphenylethane.

The paper is mainly polemical.
C. S.

Aliphatic Polynitro-compounds. JAKOB MEISENHEIMER and M. SCHWARZ (*Ber.*, 1906, **39**, 2543—2552).—Trinitroethane and potassium ethoxide react to form the potassium derivative of a substance which was regarded by Hantzsch and Rinckenberger (Abstr., 1899, i, 404) as ethyl *aci*-dinitroethane, $O:N(OEt)(OK)\cdot CHMe\cdot NO_2$, and by Meisenheimer (Abstr., 1903, i, 223) as dinitrodiethyl ether,

$$OEt\cdot CH_2\cdot C(NO_2):NO\cdot OK.$$

That the latter view is correct is proved by the following considerations. The substance, after crystallisation from alcohol, has the composition $C_4H_7O_5N_2K$, forms a bromine *derivative*, $C_4H_7O_5N_2Br$, which is a colourless oil boiling at 103—104° under 13 mm. pressure, and by acidification yields *dinitrodiethyl ether*, $C_4H_8O_5N_2$, a heavy, colourless oil which boils at 100° under 11 mm. pressure.

The potassium derivative of the corresponding methyl dinitroethyl ether, $OMe\cdot CH_2\cdot C(NO_2):NO\cdot OK$, is reduced by tin and hydrochloric acid to methoxyacetic acid, $OMe\cdot CH_2\cdot CO_2H$. A reaction similar to the one in question takes place between trinitroethane and potassium cyanide in methyl-alcoholic solution, whereby the potassium salt of aci-*dinitropropionitrile*, $CN\cdot CH_2\cdot C(NO_2):NO\cdot OK$, is obtained; it separates from water in glistening, yellow leaflets, and by treatment with aqueous silver nitrate yields the explosive *silver* salt, $C_3H_2O_4N_3Ag$, which forms yellow needles. The *nitrile*, $CN\cdot CH_2\cdot CH(NO_2)_2$, obtained by acidifying the potassium derivative, is an oil which cannot be distilled without decomposition, but by keeping in a vacuum over sulphuric acid it solidifies to a mass of deliquescent, yellow needles.

Methyl ββ-dinitropropionate, $CH(NO_2)_2\cdot CH_2\cdot CO_2Me$, is obtained by treating potassium dinitropropionitrile, suspended in methyl alcohol, with hydrogen chloride; the crude ester is dissolved in methyl alcohol, cooled, and slowly treated with 10 per cent. methyl-alcoholic potash, and the *potassium* derivative, $C_4H_5O_6N_2K$, which separates as an amorphous precipitate, is crystallised from water and methyl alcohol and acidified, when the pure methyl ester is obtained as a colourless oil. Dinitropropionitrile is hydrolysed by concentrated hydrochloric acid, forming dinitropropionic acid, a viscous, green oil, which explodes when heated; the potassium salt is precipitated from alcoholic solution as a yellow, flocculent precipitate.

By treatment with 10 per cent. hydrogen peroxide, potassium dinitropropionitrile yields cyanoacetic acid, which was identified by its conversion into malonic acid. When a methyl-alcoholic solution of trinitroethane is treated with an alkaline solution of hydroxylamine, a quantitative yield of potassium *aci*-dinitroethane is obtained. *Iodotrinitromethane*, $CI(NO_2)_3$, obtained from iodine and silver nitroform in ethereal solution, forms yellow leaflets, melts at 55—56°, distils and slightly decomposes at 48—48·5° under 13 mm. pressure, and undergoes decomposition when quickly heated (compare preceding abstract). C. S.

Some Synthetical Reactions of Pinacolin. LOUIS HENRY (*Compt. rend.*, 1906, **143**, 20—22).—Pinacolin reacts with magnesium methyl bromide to form pentamethylethanol in the form of its crystalline hydrate, $CMe_3\cdot CMe_2\cdot OH,H_2O$ (compare Butleroff, this Journal, 1875, 1248), which can also be prepared from acetone by the action of magnesium *ter*-butyl chloride. Pinacolin combines with anhydrous hydrogen cyanide, or with a 25 per cent. solution of the acid, to form β-cyano-$\gamma\gamma$-dimethylbutan-β-ol, $CMe_3\cdot CMe(OH)\cdot CN$ (compare Carlinfanti, Abstr., 1898, i, 234; 1899, i, 671), which crystallises in white needles, melts at 94° (Carlinfanti found 82—87°), is insoluble in water, and very soluble in ether, alcohol, light petroleum, or glacial acetic acid; the *acetyl* derivative, $CMe_3\cdot CMe(OAc)\cdot CN$, is a pale yellow, slightly viscous liquid, possessing a peculiar sour-sweet odour; it boils at 228—230° under 770 mm. pressure, has a sp. gr. 0·9535 at 20°, and n_D 1·43091. M. A. W.

Preparation of Pinacone. ARNOLD F. HOLLEMAN (*Rec. trav. chim.*, 1906, **25**, 206—207).—A modification of Couturier and Meunier's method for the preparation of pinacone (Abstr., 1905, i, 326). When a solution of 20 grams of mercuric chloride in 200 grams of dry acetone is allowed to drop slowly on to 20 grams of bright magnesium wire in a reflux apparatus, a violent action occurs and the acetone boils; the reaction is completed by heating the contents of the flask until all the acetone has disappeared; this requires from one to two hours; water is then added and the pinacone separated from the mixture by distillation; the yield is 70 grams. M. A. W.

Preparation of the Chlorohydrin, the Oxide, and an Unsaturated Alcohol from Normal Diprimary Decylene Glycol [Decan-$\alpha\kappa$-diol]. LEO ALBERTI and BRONISLAV SMIECIUSZEWSKI (*Monatsh.*, 1906, **27**, 411—419. Compare Scheuble, Abstr., 1904, i, 3).—The *chlorohydrin*, $CH_2Cl\cdot[CH_2]_8\cdot CH_2\cdot OH$, prepared by heating decylene glycol with hydrochloric acid of sp. gr. 1·19 in a reflux apparatus on the water-bath, is obtained as a strongly refracting, colourless oil which boils at 164—165° under 20 mm. pressure, and is readily soluble in ether, alcohol, benzene, or light petroleum. When heated with powdered, freshly fused sodium hydroxide, the chlorohydrin yields a mixture of the corresponding oxide and an unsaturated alcohol.

Decamethylene oxide, $C_{10}H_{20}O$, is obtained as a transparent liquid which boils at 181°, does not form an additive compound with bromine, and is not acted on by zinc ethyl at 180°, or by water at 200°, but yields the chlorohydrin when heated with concentrated hydrochloric acid at 110°.

The *unsaturated alcohol*, $C_{10}H_{20}O$, boils at 234—238°, and when heated with acetic anhydride and sodium acetate at 130° forms an *acetate*, $C_{12}H_{22}O_2$, which boils at 242—246° and forms an additive *compound* with 1 mol. of bromine. G. Y.

$\alpha\beta\beta$-Trichloroethyl Ether. II. GIUSEPPE ODDO and EFISIO MAMELI (*Gazzetta*, 1906, **36**, i, 480—490. Compare Abstr., 1904, i, 280).—The action on $\alpha\beta\beta$-trichloroethyl ether of an aqueous solution of potassium hydroxide or ethylamine or sodium hydrogen sulphite yields the same products as, but proceeds more rapidly than, the action of water.

The first phases of the action of dry ammonia on αββ-trichloroethyl ether proceed according to the equations: (1) $CHCl_2 \cdot CHCl \cdot OEt + 2NH_3 = CHCl_2 \cdot CH(NH_2) \cdot OEt + NH_4Cl$; (2) $2CHCl_2 \cdot CH(NH_2) \cdot OEt = CHCl_2 \cdot CH(OEt)_2 + CHCl_2 \cdot CH(NH_2)_2$. The last compound is, however, unstable, and gives rise to resinous, complex nitrogen compounds of basic character.

Powdered magnesium has little action on αββ-trichloroethyl ether, either by itself or in presence of a solvent. When benzene is used as solvent and the mixture is heated in a reflux apparatus, aldehydic vapours are evolved and dichloroacetal and a small quantity of a product of low boiling point are formed.

Zinc dust acts readily on αββ-trichloroethyl ether with formation of dichloroaldehyde and large quantities of hydrogen chloride, but no organo-zinc compound of the formula $CHCl_2 \cdot CH(OEt) \cdot ZnCl$ could be obtained.

Reduction of the trichloro-ether by powdered zinc or magnesium and a stream of dry hydrogen chloride, or by zinc and acetic acid, gives mainly dichloroaldehyde, together with a fraction boiling at 80—90° under 10 mm. pressure, which is probably ββ-dichloroethyl ether.

Dichloromonothioacetal, $SEt \cdot CH(OEt) \cdot CHCl_2$, prepared by the interaction of αββ-trichloroethyl ether (1 mol.) and ethyl mercaptan (1 mol.), boils at 110—125° under 20—30 mm. pressure.

Phenylethyldichloroacetal, $OEt \cdot CH(OPh) \cdot CHCl_2$, obtained by the action of sodium phenoxide on αββ-trichloroethyl ether, boils at 165—170° under 40 mm. pressure, reacts energetically with nitric acid, combines with bromine giving a white compound, decolorises permanganate, dissolves in alcohol, and readily decomposes even in a closed vessel in the dark.

αββ-Trichloroethyl ether (1 mol.) combines with pyridine (1 mol.), forming a substance which, with platinum chloride, gives a *compound*, $(CHCl_2 \cdot CHCl \cdot OEt, C_5NH_5)_2, PtCl_4$, crystallising from dilute hydrochloric acid in orange-yellow needles, melting and decomposing at 208—209°, and, with gold chloride, a yellow *compound*,

$$(CHCl_2 \cdot CHCl \cdot OEt, C_5NH_5)_2, AuCl_3,$$

melting at 92—93°. T. H. P.

Course of the Decomposition of Mixed Aliphatic Ethers by Hydrogen Iodide. Arthur Michael and Francis D. Wilson (*Ber.*, 1906, **39**, 2569—2577. Compare da Silva, this Journal, 1876, i, 60; Lippert, Abstr., 1893, i, 620).—When methyl propyl ether is treated with hydrogen iodide at 0°, an additive *compound*, $C_4H_{10}O,HI$, is formed, which is subsequently decomposed. The products are well washed with water, dried with phosphoric oxide, and fractionated, whereby mainly methyl iodide is obtained, the very small quantity of propyl iodide formed being identified in the form of silver propionate.

Ethyl propyl ether yields a similar additive *compound*, $C_5H_{12}O,HI$, which is decomposed at 100°; from the products, after treatment as above, ethyl and propyl iodides were isolated. The additive *compound*, $C_6H_{14}O,HI$, obtained from propyl *iso*propyl ether, is decomposed at 100°, and the products treated as before.

The mixed propyl and *iso*propyl iodides are converted into the aldehyde and ketone respectively, and identified in the form of the hydrazones.

From considerations of the heats of formation of the alkyl iodides, and also of the energy required to separate the different alkyl groups from oxygen, the authors conclude that an ether containing methyl and a primary or secondary alkyl group will yield methyl iodide and alkylcarbinol by treatment with hydrogen iodide, whilst methyl alcohol and a tertiary alkyl iodide will result from an ether containing the methyl and a tertiary alkyl group. Moreover, an ether containing two primary, two secondary, or two such mixed alkyl groups will yield a mixture of haloids and alcohols containing each of the alkyl groups. C. S.

Electrolytic Preparation of Alkyloxides and Alkylcarbonates. Béla Szilárd (*Zeit. Elektrochem.*, 1906, **12**, 393—395).—When a solution of sodium ethoxide (4 per cent.) in pure anhydrous alcohol is electrolysed with platinum electrodes and a current density just sufficient to produce a small evolution of gas at the anode, sodium ethyl carbonate is formed as a solid deposit at the anode. The yield is about one-seventh of the theoretical quantity. Sodium methyl carbonate is formed in a similar way. Using a magnesium anode, magnesium ethyl (or methyl) carbonate is obtained. Using a lead anode, a one per cent. sodium methoxide solution, and a small current density, lead methoxide, $Pb(OMe)_2$ is formed; with higher current densities, salts containing increasing quantities of carbon dioxide are produced. Copper methoxide, $Cu(OMe)_2$, was obtained in a similar way. T. E.

Preparation of the Anhydrides of Monobasic Organic Acids. Verein für Chemische Industrie in Frankfurt (D.R.-P. 167304).—When a mixture of chlorine and sulphur dioxide containing a slight excess of the latter gas is passed into a cooled intimate mixture of anhydous sodium and calcium acetates, acetic anhydride is produced and obtained by distilling the mixture, preferably under reduced pressure (compare Abstr., 1906, i, 3). G. T. M.

Reactions of Double Decomposition between Alcohols and Esters. Giuseppe Bruni and Angelo Contardi (*Atti R. Accad. Lincei*, 1906, [v], **15**, i, 637—644).—The authors have heated mixtures, in molecular proportions, of menthol with ethyl acetate, ethyl benzoate, ethyl oxalate, or ethyl malonate, in order to determine whether any double decomposition takes place under these conditions, the changes being followed by means of the rotatory power. With ethyl acetate, no change occurs after heating for ten hours at 100°, and the same is the case with ethyl benzoate after twelve hours' heating at 80°. With ethyl oxalate and ethyl malonate, however, double decomposition proceeds at an appreciable velocity when they are heated at 100° with menthol.

With ethyl acetoacetate (2 mols.) and menthol (1 mol.), or with menthyl acetoacetate (1 mol.), ethyl alcohol (1 mol.), and ethyl acetoacetate (1 mol.), double decomposition takes place, equilibrium being reached after heating at 100° for twenty-four hours, when 57·6 per cent. of the menthol has been transformed into menthol acetoacetate. At 79·9°, however, equilibrium is not attained, even after 155 hours, although the final condition of equilibrium is the same at this temperature as at 100°. The values of K, calculated according to the equation for a bimolecular reaction, are not constant, but decrease as the time increases. T. H. P.

Preparation of Solid Fatty Acids. CARL DREYMANN (D.R.-P. 166610).—The ordinary process for obtaining solid fatty acids from the unsaturated fatty acids or their glycerides depends on the treatment of these substances with strong sulphuric acid at 60—120°, the subsequent washing out of this acid with water or brine solution, and the distillation of the product. The final operation is attended by a certain amount of destructive action due to the decomposition of the hydroxystearic acid which is present. This effect is due to the presence of sulphuric acid, which is tenaciously retained by the organic matter in spite of the washing with water. The distillation may, however, be greatly improved by the introduction of some oxide, carbonate, or other acid-fixing substance, which neutralises the mineral acid, and thus prevents the formation of hydrocarbons and tar.

G. T. M.

Measurements of Affinity of Monobasic Unsaturated Fatty Acids. FRITZ FICHTER and HERMANN MUELLER (*Annalen*, 1906, **348**, 256—259. Compare Fichter and Pfister, Abstr., 1904, i, 965).—The affinity constants of a number of monobasic $\alpha\beta$- and $\beta\gamma$-unsaturated fatty acids have been measured by means of the inversion of sucrose and of the hydrolysis of methyl acetate; the results, which are given in the following table, confirm Fichter and Pfister's observation that the $\beta\gamma$-unsaturated acids have the larger affinity constants:

	Inversion of sucrose. $K \times 10^{-4}$.	Hydrolysis of methyl acetate. $K \times 10^{-4}$.
Butyric acid	0·0569	0 0206
Crotonic acid	0·0723	0·0320
Vinylacetic acid	0·0941	0·0540
n-Valeric acid	0·0545	0·0164
$\alpha\beta$-Pentenoic acid	0·0691	0·0170
$\beta\gamma$-Pentenoic acid	0·1738	0·0668
α-Methyl-$\alpha\beta$-pentenoic acid	0·0284	0·0235
α-Methyl-$\beta\gamma$-pentenoic acid	0·0757	0·0325

α-Ethyl-$\alpha\beta$-pentenoic acid has the dissociation constant $K = 0·00205$, and α-ethyl-$\beta\gamma$-pentenoic acid, $K = 0·00339$.

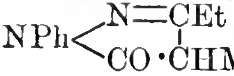
The heat of combustion of α-methyl-$\alpha\beta$-pentenoic acid is 795·7 Cal., whilst that of α-methyl-$\beta\gamma$-pentenoic acid is 797·9 Cal. (compare Thiele, Abstr., 1899, i, 554). G. Y.

Transformations of Salts of Pyruvic Acid. IV. ANNE W. K. DE JONG (*Rec. trav. chim.*, 1906, **25**, 229—232. Compare Abstr., 1902, i, 72; 1903, i, 146; 1904, i, 550).—Barium parapyruvate, $C_6H_6O_6Ba,4H_2O$, prepared by the condensation of barium pyruvate spontaneously or by means of baryta, loses $3H_2O$ when exposed over sulphuric acid. The impurity present in small quantity in barium parapyruvate which has been prepared by the action of potassium cyanide on barium pyruvate is sparingly soluble in boiling water, and dissolves in hydrochloric acid; the solution on evaporation over sulphuric acid and quicklime deposits crystals of a *compound* which has the empirical formula $C_7H_8O_7,\frac{1}{2}H_2O$, and is probably the $\alpha\gamma$-lactone of $\alpha\gamma$-dihydroxybutane-$\alpha\alpha\gamma$-tricarboxylic acid,

$$CO_2H\cdot C(OH)<\begin{matrix}CH_2\cdot CMe\cdot CO_2H\\ CO-O\end{matrix}.$$

The hydrated compound softens at 100° and decomposes at 180°, the anhydrous compound decomposes at 195°. M. A. W.

Derivatives of Ethyl Propionylpropionate. OSKAR EMMERLING and L. KRISTELLER (*Ber.*, 1906, **39**, 2450—2455).—When ethyl propionylpropionate is heated with phenylhydrazine on the water-bath and finally at 140°, 1-*phenyl*-4-*methyl*-3-*ethylpyrazolone*,



$$NPh<\begin{matrix}N{=}CEt\\ CO\cdot CHMe\end{matrix},$$

is obtained; it melts at 112·5° and yields the corresponding salt with hot dilute hydrochloric or sulphuric acid. When heated with methyl iodide and methyl alcohol at 110°, it forms 1-*phenyl*-2 : 4-*dimethyl*-3-*ethylpyrazolone*, $C_{13}H_{16}ON_2$, which melts at 37·5°, boils at 208—210° under 18 mm. pressure, and forms a *platinichloride*, $2C_{13}H_{16}ON_2,H_2PtCl_6,2H_2O$. The interaction of chloroform and the reaction product of sodium and ethyl propionate leads to the formation of *β-ethoxymethylacrylic acid*, $OEt\cdot CH{:}CMe\cdot CO_2H$, which separates from light petroleum in leaflets or long needles and melts at 106—107°.

$$COEt\cdot CMeNa\cdot CO_2Et + CH(OEt)_3 = COEt\cdot CMe(CO_2Et)\cdot CH(OEt)_2.$$
$$COEt\cdot CMe(CO_2H)CH(OEt)_2 + H_2O = CO_2H\cdot CMe{:}CH\cdot OEt + 2EtOH.$$

The *potassium*, *barium*, *calcium*, *silver*, and *cadmium* salts are mentioned; the *ethyl* ester boils at 198—199° and has an aromatic odour.

The acid is stable towards cold dilute mineral acids, but by warming yields carbon dioxide, alcohol, and propaldehyde; it absorbs bromine to form a yellow, crystalline additive *compound*, $C_6H_{10}O_3Br_2$.

The constitution of the acid has been verified by its production from β-bromomethylacrylic acid, sodium ethoxide, and alcohol at 130—140°.

Hantzsch and Wohlbrück's acid, $C_6H_8O_3$ (Abstr., 1887, i, 717), obtained by warming ethyl bromopropionylpropionate, melts, not at 106—108°, but at 124°, and does not yield β-methoxymethylacrylic acid when reduced. C. S.

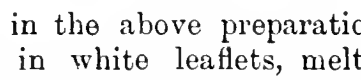
Crystallographic Description of Alkali Cobaltioxalates. H. COPAUX (*Chem. Centr.*, 1906, i, 1604; from *Bull. Soc. franç. Min.*, **29**, 67—76. Compare Abstr., 1902, i, 586).—$(NH_4)_6Co_2(C_2O_4)_6,6H_2O$

is monoclinic and isomorphous with the ammonium oxalates of aluminium, chromium, and iron [$a:b:c = 1{\cdot}0017:1:0{\cdot}3929$; $\beta = 92°44'$]. $K_6Co_2(C_2O_4)_6,7H_2O$, triclinic [$a:b:c = 0{\cdot}5963:1:0{\cdot}6590$; $\alpha = 88°22'$, $\beta = 91°42'$, $\gamma = 101°23'$]. $Rb_6Co_2(C_2O_4)_6,8H_2O$, rhombic [$a:b:c = 1{\cdot}1485:1:2{\cdot}5960$]. $Na_6Co_2(C_2O_4)_6,10H_2O$ is monoclinic and isomorphous with the corresponding oxalates of aluminium, chromium, and iron [$a:b:c = 1{\cdot}398:1:1{\cdot}293$]. $Li_6Co_2(C_2O_4)_6,12H_2O$ is triclinic and is isomorphous with the lithium oxalates of aluminium and chromium [$a:b:c = 1{\cdot}0177:1:0{\cdot}7885$; $\alpha = 94°22'$, $\beta = 81°$, $\gamma = 109°4'$]. $K_5Na_{19}Co_8(C_2O_4)_{24},32H_2O$ crystallises in pseudoregular octahedra and is isomorphous with the corresponding aluminium and chromium oxalates. $Rb_3Na_3Co_2(C_2O_4)_6,5H_2O$ is monoclinic and isomorphous with the corresponding aluminium oxalate [$a:b:c = 1{\cdot}2211:1:0{\cdot}8758$; $\beta = 91°38'$]. The crystals of $(NH_4)_3Na_3Co_2(C_2O_4)_6,7H_2O$ are monoclinic, but so strongly striated that they cannot be measured.

E. W. W.

Ethyl Dioximidosuccinate. André Wahl (*Compt. rend.*, 1906, **143**, 56—58).—Ethyl dioximidosuccinate, prepared by the action of hydroxylamine hydrochloride on ethyl dioxysuccinate (Anschütz and Parlato, Abstr., 1892, 1181), is dimorphous, crystallising from a mixture of ether and light petroleum in small, transparent prisms, and in large, transparent crystals which become opaque and white when removed from the mother liquor; the two modifications melt and decompose at 196° and are mutually convertible by the action of solvents. It is soluble in boiling water, alcohol, or ether, and insoluble in cold water, and differs from the compound described by Beckh (Abstr., 1897, i, 213), which is soluble in water and melts at 162°. Ethyl glyoxime-peroxide-dicarboxylate, $C_8H_{10}O_6N_2$, is obtained together with a little ethyl dinitroacetate when ethyl dioximidosuccinate is oxidised with fuming nitric acid, and when treated with ammonia yields the amide, $(CONH)_4$, melting at 250° (compare Pröpper, Abstr., 1883, 573; Cramer, Abstr., 1892, 699; and Bouveault and Bongert, Abstr., 1903, i, 145).

Ethyl 4-iso*nitroso*iso*oxazolone-3-carboxylate*,



$$CO_2Et{\cdot}C{<}\begin{matrix}C(NOH){\cdot}CO\\ |\\ N{-}{-}{-}{-}{-}O\end{matrix},$$

formed as a by-product in the above preparation of ethyl dioximidosuccinate, crystallises in white leaflets, melts and decomposes at 160—165°, is sparingly soluble in water, and yields a characteristic fugitive violet coloration with alkalis.

M. A. W.

Electrolytic Decomposition of Dicarboxylic Acids: Adipic Acid. B. Lino Vanzetti (*Atti R. Accad. Lincei*, 1906, [v], **15**, i, 574—578. Compare Abstr., 1904, i, 141).—In the electrolysis of potassium adipate, a large quantity of carbon dioxide is evolved at the anode, so that the decomposition of the acid is far more profound than has been formerly supposed. The mean and almost constant composition of the gases is: carbon dioxide, 25; unsaturated hydrocarbons, 1·5; oxygen, 12; carbon monoxide, 1·5; and hydrogen, 60 per cent. The unsaturated hydrocarbons consist of butylenes of the formulæ $CH_2Me\cdot CH\colon CH_2$ and $CHMe\colon CHMe$. The characteristic ethereal odour is due to the secondary formation of alcohols and ethereal salts.

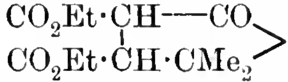
T. H. P.

β-Methylglutaconic Acids. Fritz Fichter and Julius Schwab (*Annalen*, 1906, **348**, 251—256. Compare Feist, this vol., i, 334).—The action of ethyl β-chlorocrotonate or ethyl β-chloro*iso*crotonate on ethyl sodiomalonate leads to the formation of ethyl β-methylcarboxyglutaconate, which boils at 163—165° under 12 mm. pressure, and on hydrolysis with barium hydroxide yields a mixture of *cis*- and *trans*-β-methylglutaconic acids. The *cis*-acid melts at 152°, has a dissociation constant $K = 0·0129$, and forms salts which crystallise more readily than do those of the *trans*-acid, which melts at 116°, has the dissociation constant $K = 0·0139$, and is converted partially into the *cis*-form when boiled with aqueous sodium hydroxide (compare Feist, *loc. cit.*). Barium *trans*-β-methylglutaconate crystallises with $5H_2O$ ($6H_2O$; Genvresse, *Ann. Chim. Phys.*, 1891, [vi], **24**, 88). The *anilide* of the *trans*-acid, $C_{12}H_{11}O_2N$, melts at 166° and boils at 186° under 14 mm. pressure; the p-*toluidide*, $C_{13}H_{13}O_2N$, crystallises in long needles, melts at 164°, and boils at 236—240° under 15 mm. pressure.

αβ-Dibromo-β-methylglutaric acid, $C_6H_8O_4Br_2$, formed by the action of bromine under the influence of sunlight on *trans*-β-methylglutaconic acid dissolved in a mixture of glacial acetic acid and chloroform, crystallises from a mixture of chloroform and light petroleum and melts at 145°.

G. Y.

Condensation of Ethyl ββ-Dimethylglycidate with Ethyl Sodiomalonate. Synthesis of Terebic and Pyroterebic Acids. Albin Haller and Gustave Blanc (*Compt. rend.*, 1906, **142**, 1471—1473).—*γγ-Dimethyl-αβ-dicarbethoxybutyrolactone* (4-*methyl*-2:3-*dicarbethoxypentan*-4-*olid*),



$$\left.\begin{array}{l}CO_2Et\cdot CH{-}{-}CO\\ \qquad\quad |\\ CO_2Et\cdot CH\cdot CMe_2\end{array}\right> O,$$

obtained by the condensation of ethyl ββ-dimethylglycidate (Darzens, Abstr., 1905, i, 116) with ethyl sodiomalonate, boils at 174° under 12 mm. pressure, crystallises from a mixture of ether and light petroleum in large prisms, melts at 46°, and is converted quantitatively into terebic acid by boiling with hydrochloric acid. The terebic acid was characterised by its conversion into pyroterebic acid and *iso*hexolactone by the action of heat; the phenylhydrazide of pyroterebic acid melts at 106°.

Attempts to effect the condensation of ethyl αββ-trimethylglycidate with ethyl sodiomalonate were unsuccessful, owing probably to steric hindrance.

M. A. W.

Organic Thio-acids. II. Einar Biilmann (*Annalen*, 1906, **348**, 120—132. Compare Abstr., 1905, i, 625; Holmberg, Abstr., 1905, i, 323; Klason and Carlson, this vol., i, 232).—Thioglycollic acid is prepared by dissolving xanthoacetic acid in cooled 25 per cent. aqueous ammonia; after twenty-four hours, the mixture is extracted with ether and heated at 112°, made alkaline with ammonia, and again extracted with ether and left overnight in contact with zinc filings; it boils at 103—105° under 14 mm. pressure, and has a sp. gr. 1·326 at 17·3°.

Thiolactic acid is prepared from *a*-xanthopropionic acid; it boils at 98·5—99° under 14 mm. pressure, and, when cooled with ice-water, crystallises, melting at about 10°.

Thiohydracrylic acid, prepared from *β*-xanthopropionic acid, forms white crystals, melts at 16·8°, boils at 110·5—111·5° under 15 mm. pressure, decomposes when heated under the ordinary pressure, and has a sp. gr. 1·218 at 20·8°.

*a-Xantho*iso*butyric acid*, $OEt·CS·S·CMe_2·CO_2H$, prepared from potassium xanthate and sodium *iso*butyrate, forms white crystals and melts at 102—103°. When heated with ammonia, it yields *a*-thiol*iso*butyric acid, which is crystalline, melts at 47°, boils at 101—102° under 15 mm. pressure, gives an intense indigo-blue coloration with ferric chloride, changing to reddish-violet on addition of ammonia, forms with copper sulphate a yellow, with mercuric chloride or silver nitrate a white precipitate, and is oxidised by iodine, forming *a-dithiodi*iso*butyric acid*, $C_8H_{14}O_4S_2$, separating from hot water in colourless crystals.

Disulphidedisuccinic acid, $S_2[CH(CO_2H)·CH_2·CO_2H]_2$, prepared by the oxidation of thiomalic acid with ferric sulphate and aqueous ammonia, is obtained as a white, crystalline residue. G. Y.

Organic Thio-acids. III. EINAR BIILMANN (*Annalen*, 1906, **348**, 133—143. Compare preceding abstract; Abstr., 1905, i, 625).—A reply to Holmberg (Abstr., 1905, i, 324).

Trithiocarbodiglycollic acid is formed by the action of sodium chloroacetate on potassium xanthate in hot aqueous solution or by heating alkali xanthoacetates with water. It is decomposed to only a small extent when boiled with water. The sodium salt crystallises with $2\frac{1}{2}H_2O$.

Carbethoxythioglycollic acid, $OEt·CO·S·CH_2·CO_2H$, prepared by the action of potassium thiocarbonate on potassium xanthate, forms colourless, transparent crystals, melts at 28—29°, boils at 110—115° under 20 mm. pressure, is extremely hygroscopic, and is decomposed by alcoholic potassium hydroxide, yielding alcohol, carbon dioxide, and thioglycollic acid, or by alcoholic ammonia, yielding thioglycollic acid and xanthamide. The *potassium* salt, $C_5H_7O_4SK$, was analysed.

The action of ammonia on xanthoacetic acid leads to the formation of xanthamide, that of aniline to the formation of xanthanilide and *s*-diphenylcarbamide.

The formation of the reddish-yellow, crystalline potassium trithiocarbonate, $C_3H_2O_2S_8K_6$, by the successive action of hydrogen sulphide and carbon disulphide on alcoholic potassium hydroxide is confirmed.
G. Y.

Sulphoacetic Acid. II. Sulphoacetic Acid and Aromatic Amines. OTTO STILLICH (*J. pr. Chem.*, 1906, [ii], **74**, 51—56. Compare this vol., i, 552).—*Aniline sulphoacetate*, $(NH_2Ph)_2,C_2H_4O_5S$, formed by the action of aniline on aniline hydrogen sulphoacetate, melts at

125—151°, decomposes into aniline and sulphoacetic acid when recrystallised from alcohol, and when highly heated yields *aniline acetanilide-ω-sulphonate*, $NHPh\cdot CO\cdot CH_2\cdot SO_3H,NH_2Ph$, which is formed quantitatively by heating aniline with sulphoacetic acid at 200°; it crystallises from absolute alcohol in long prisms and melts at 229—231°. The *sodium* salt, $NHPh\cdot CO\cdot CH_2\cdot SO_3Na,H_2O$, forms nacreous, quadratic leaflets and melts at 283—284°.

p-*Phenetidine sulphoacetate*, $(OEt\cdot C_6H_4\cdot NH_2)_2,C_2H_4O_5S$, crystallises in long, white needles, melts at about 146°, forming a turbid liquid which becomes clear at about 170°, and when highly heated forms p-*phenetidine acetyl*-p-*phenetidine-ω-sulphonate*,

$$OEt\cdot C_6H_4\cdot NH\cdot CO\cdot CH_2\cdot SO_3H,NH_2\cdot C_6H_4\cdot OEt;$$

this crystallises in needles, commences to sinter at 224°, and melts at 233—240°. The *sodium* salt, $OEt\cdot C_6H_4\cdot NH\cdot CO\cdot CH_2\cdot SO_3Na,2H_2O$, crystallises in needles and melts at about 270°, forming a turbid liquid which is not clear at 290°.

p-*Anisidine acetyl*-p-*anisidine-ω-sulphonate* forms matted needles, sinters at 220°, and melts at 224—227°. The *sodium* salt,

$$OMe\cdot C_6H_4\cdot NH\cdot CO\cdot CH_2\cdot SO_3Na,H_2O,$$

crystallises in nacreous, rectangular leaflets, commences to soften at about 269°, and gradually decomposes when more highly heated.

The *salt*, $C_7H_7\cdot NH\cdot CO\cdot CH_2\cdot SO_3H,NH_2\cdot C_7H_7$, formed from *o*-toluidine, crystallises in blue, pointed needles, melting at 189—191°; the *sodium* salt, $C_9H_{10}O_4SNa,H_2O$, forms prismatic needles and melts at 223—224°.

The *salt*, $C_{10}H_7\cdot NH\cdot CO\cdot CH_2\cdot SO_3H,C_{10}H_7\cdot NH_2$, formed from *α*-naphthylamine, decomposes on recrystallisation; the *sodium* salt, $C_{10}H_7\cdot NH\cdot CO\cdot CH_2\cdot SO_3Na$, forms matted needles and melts at 285—287°. G. Y.

Preparation of Aldehydes and Ketones from Alcohols.

W. LANG (D.R.-P. 166357).—The manganic salts are found to be very useful in oxidising alcohols to aldehydes and ketones, inasmuch as the reaction is not carried further when the oxidising agent is in excess.

Manganous ammonium sulphate, $2MnSO_4,(NH_4)_2SO_4$, obtained in anhydrous crystals by adding excess of ammonium sulphate to a hot acid solution of manganous sulphate, is decomposed by cold water into the double sulphate, $MnSO_4(NH_4)_2SO_4$, and manganous sulphate, but when electrolysed in an anode cell lined with lead, the current density being 3·5 amperes per sq. cm., it gives rise to manganic ammonium alum, which is hydrolysed by water, yielding manganic hydroxide.

The mixture thus obtained is employed in oxidising methyl alcohol to formaldehyde, 2·4 parts of the latter being obtained from 4 parts of the alcohol. In a similar manner, 17 parts of menthol yield 14 parts of menthone. G. T. M.

Decomposition of Formaldehyde by the Silent Discharge.

FRANZ RUSS (*Zeit. Elektrochem.*, 1906, **12**, 412—413).—The silent discharge was passed through the vapour of formaldehyde at 150° and the formation of carbon monoxide and hydrogen observed. T. E.

Preparation of a Solid Modification of Chloral. SIMON GÄRTNER (D.R.-P. 170534).—Chloral hydrate is left for several hours in contact with about half its weight of concentrated sulphuric acid until a white, pasty mass is formed. The acid is then poured off and the residue introduced into well-cooled dilute hydrochloric or sulphuric acid; the product, which now becomes solid, is washed and dried over concentrated sulphuric acid. This product can also be obtained from chloral alcoholate; it is only sparingly soluble in water and becomes quite insoluble when acid is added. It can be employed as an anæsthetic or a hypnotic, and, unlike chloral hydrate, it is devoid of any irritating action on the mucous membrane of the stomach.

G. T. M.

Preparation of Aldehydes, Alcohols, and Acids. CHEMISCHE FABRIK FLÖRSHEIM, H. HOERDLINGER (D.R.-P. 167137).—The volatile product obtained by blowing air, oxygen, or an ozonised mixture of these gases through heated oils or fats consists of a mixture of the lower aldehydes, alcohols, and aliphatic acids (from C_6 onwards).

Castor oil was heated to 160° and a current of air introduced; a vigorous reaction ensued, raising the temperature to 220°; the distillate was collected and the oily portion mixed with petroleum and sodium hydrogen sulphite solution and saturated with sulphur dioxide until two clear layers separated. The petroleum extract when shaken with dilute aqueous sodium hydroxide yielded sodium *n*-hexoate and *n*-heptoate, and *n*-heptyl and *n*-octyl alcohols. The sodium hydrogen sulphite solution furnished heptaldehyde.

Similar results were obtained with linseed and rape-seed oils.

G. T. M.

Formation of Glycerose. NAZARENO TARUGI (*Gazzetta*, 1906, **36**, i, 332—347. See this vol., ii, 631).

[Alkylenediamine Chromium Compounds.] PAUL PFEIFFER (*Annalen*, 1906, **346**, 26—81. See this vol., ii, 614).

Antimonichlorides of Dichloro-salts. PAUL PFEIFFER and M. TAPUACH (*Zeit. anorg. Chem.*, 1906, **49**, 437—440. Compare Abstr., 1904, ii, 41).—With the object of elucidating the constitution of the green double chloride of antimony and chromium, $CrCl_3,SbCl_5,10H_2O$, described by Weinland and Feige (Abstr., 1903, ii, 218), the authors have prepared and examined two complex antimonichlorides of analogous constitution. The *compound*, $[Cr,C_4H_8N_2H_2,Cl_2][SbCl_5]$, prepared by the action of antimony pentachloride on violet cis-*dichlorodiethylenediamine chromium chloride*, $[Cr,C_4H_8N_2H_2,Cl_2]Cl$, dissolved in hydrochloric acid, forms violet crystals. The *compound*, $[Co\cdot C_4H_8N_2H_2\cdot Cl_2][SbCl_5]$, obtained in a similar manner from trans-*dichlorodiethylenediamine cobalt chloride*, $[Co\cdot C_4H_8N_2H_2\cdot Cl_2]Cl$, and antimony pentachloride, forms a green precipitate. The antimony was removed from these double salts by treatment with hydrogen sulphide, and from the respective filtrates derivatives of chromium and cobalt containing two atoms of chlorine were obtained, which proves the constitution to be as above. From analogy, the formula $[Cr(H_2O)_4Cl_2][SbCl_5]$ is ascribed to the double chloride of antimony and chromium in agreement with Weinland and Schmid (Abstr., 1905, ii, 326). G. S.

Compounds of Metallic Thiocyanates with Organic Bases HERMANN GROSSMANN and BERNHARD SCHÜCK (*Zeit. anorg. Chem.*, 1906, **50**, 1—20. Compare this vol., i, 7, 485).—In the present paper, compounds of ethylenediamine with thiocyanates and other salts of bivalent metals are described, and one or two compounds containing α- and β-naphthylamine have also been prepared. In the majority of cases the compounds were obtained by the direct action of the calculated quantity of base on the salt in aqueous solution; in some cases double decomposition between potassium thiocyanate and the ethylenediamine compound of other salts has been employed. In the course of the investigation it was found that, contrary to Ostwald's opinion (Abstr., 1886, 586), free ethylenediamine, and in some cases the combined base, can be accurately estimated by titration with sulphuric acid, using methyl-orange or litmus as indicator.

Nickel Compounds.—Triethylenediaminenickel thiocyanate,

$$(Ni,3C_2H_8N_2)(SCN)_2,$$

separates from aqueous solution in violet, prismatic crystals, which melt at 253°. It is decomposed by acids with formation of the corresponding salt of ethylenediamine, and by hot potassium hydroxide, green nickel hydroxide being precipitated. *Diethylenediaminenickel thiocyanate*, $(Ni,2C_2H_8N_2)(SCN)_2$, has already been obtained by Werner (Abstr., 1899, i, 857) in two isomeric forms, which crystallise with $1H_2O$ in bluish-violet plates and in reddish-violet needles respectively. The authors confirm Werner's results except that their compounds are anhydrous; both melt at 220°. The nature of the isomerism has not been elucidated. *Ethylenediaminenickel thiocyanate*,

$$(Ni,C_2H_8N_2)(SCN)_2,$$

forms bluish-green, rhombic crystals, which melt at 275°. It is also decomposed by hot potassium hydroxide, but is not affected by ammonia. *Triethylenediaminenickel cyanide*, $(Ni,3C_2H_8N_2)(CN)_2$, prepared by the action of the molecular quantity of solid potassium cyanide on the corresponding thiocyanate, forms reddish-violet crystals, which melt at 244°. *Diethylenediaminenickel chloride*,

$$(Ni,2C_2H_8N_2)Cl_2,H_2O,$$

occurs in light blue, prismatic crystals, which melt at 157°. The triethylenediamine compound has already been prepared by Werner and Spruck (*loc. cit.*); attempts to obtain the mono-compound were unsuccessful.

Zinc and Cadmium Compounds.—Triethylenediamine zinc thiocyanate, $(Zn,3C_2H_8N_2)(SCN)_2$, forms colourless, rhombohedric crystals, which melt at 161°. The corresponding *cadmium* compound, $(Cd,3C_2H_8N_2)(SCN)_2$, forms colourless plates which melt at 138°. No other compounds of these metals were obtainable.

Copper Compounds.—The three thiocyanates were obtained by double decomposition. *Triethylenediamine copper thiocyanate*,

$$(Cu,3C_2H_8N_2)(SCN)_2,5H_2O,$$

crystallises in large, deep blue plates, which melt at 138°. The *diethylenediamine* compound, $(Cu,2C_2H_8N_2)(SCN)_2,2H_2O$, forms dark blue needles, melting at 83°, and the *mono*-compound,

$$(Cu.C_2H_8N_2)(SCN)_2,$$

slender, light blue needles. The three compounds just mentioned are not affected by potassium hydroxide or by ammonia. *Ethylenediamine-copper chloride*, $(Cu,C_2H_8N_2)Cl_2,H_2O$, crystallises in reddish-blue leaflets which melt at 158°. With excess of hydrogen chloride, it yields the double *chloride*, $(Cu,C_2H_{10}N_2)Cl_4$, in golden-yellow leaflets melting at 272°. *Triethylenediaminecopper bromide*,

$$(Cu.3C_2H_8N_2)Br_2,5H_2O,$$

forms dark blue, lustrous leaflets, the *diethylenediamine* compound, $(Cu.2C_2H_8N_2)Br_2,2H_2O$, dark blue, prismatic crystals, and the *mono-ethylenediamine* compound, $(Cu,C_2H_8N_2)Br_2,H_2O$, lustrous, green plates. *Triethylenediaminecopper acetate*, $(Cu.3C_2H_8N_2)(OAc)_2,2H_2O$, crystallises in dark blue leaflets, melting at 67°; *diethylenediamine-copper acetate*, $(Cu,2C_2H_8N_2)(OAc)_2,H_2O$, in light blue, rhombic prisms, melting at 115°; and *monoethylenediaminecopper acetate*,

$$(Cu,C_2H_8N_2)(OAc)_2,$$

in dark green, lustrous, prismatic crystals. *Monoethylenediaminecopper sulphate*, $(Cu,C_2H_8N_2)SO_4,3H_2O$, forms slender, light blue needles, which decompose on heating to 260°. Diethylenediaminecopper nitrate, $(Cu,2C_2H_8N_2)(NO_3)_2,2H_2O$, forms lustrous, dark blue leaflets and melts at 213°.

Attempts were made to prepare additive compounds with α- and β-naphthylamine, but only nickel compounds were obtained. α-*Naphthyl-aminenickel thiocyanate*, $(Ni,C_{10}H_9N)(SCN)_2$, separates from an alcoholic solution of its components as a moss-green, crystalline precipitate, which decomposes on heating above 200°. The β-compound forms a yellowish-green, crystalline precipitate, which melts about 261°. G. S.

Ethylenediammonium Double Salts. HERMANN GROSSMANN and BERNHARD SCHÜCK (*Zeit. anorg. Chem.*, 1906, **50**, 21—32. Compare Kurnakoff, Abstr., 1898, ii, 475).—These double salts are of the general type $(M,C_2H_{10}N_2)X_4$, where M is a bivalent metal and X a univalent acid group, and have been prepared either by interaction of the salt of ethylenediamine with the corresponding salt of the metal in aqueous solution, or by dissolving the ethylenediamine additive compound (see preceding abstract) in excess of the corresponding acid.

Ethylenediammonium manganothiocyanate,

$$(Mn,C_2H_{10}N_2)(SCN)_4,2H_2O,$$

occurs in long, colourless plates which melt at 186°. The corresponding *ferrous* compound, $(Fe,C_2H_{10}N_2)(SCN)_4,4H_2O$, forms long, brown needles which become oxidised in the air; the *nickel* compound, $(Ni,C_2H_{10}N_2)(SCN)_4,4H_2O$, occurs in green, prismatic crystals and melts at 95°; the *cobalt* compound, $(Co,C_2H_{10}N_2)(SCN)_4,2H_2O$, in slender, dark blue needles, melting at 82°; the *zinc* compound,

$$(Zn,C_2H_{10}N_2)(SCN)_4,4H_2O,$$

in slender, colourless needles melting at 123°; and the *cadmium* compound, $(Cd,C_2H_{10}N_2)(SCN)_4$, in large, colourless, octahedral crystals which melt at 182°.

Ethylenediammonium mercurithiocyanate, $(Hg,C_2H_{10}N_2)(SCN)_4$, forms colourless, prismatic crystals, which melt at 120°. The *compound*, $(Hg_2,C_2H_{10}N_2)(SCN)_6$, also forms colourless crystals which melt about 114°.

Ethylenediammonium cobaltochloride, $(Co,C_2H_{10}N_2)Cl_4,6H_2O$, separates from aqueous solution in lustrous, light green needles which melt at 254°. The corresponding *bromide*, $(Co,C_2H_{10}N_2)Br_4,2H_2O$, occurs in slender, light blue needles. *Ethylenediammonium cupribromide*, $(Cu,C_2H_{10}N_2)Br_4,5H_2O$, occurs in black, lustrous leaflets which melt at 242°.

Ethylenediammonium cadmium chloride, $(Cd,C_2H_{10}N_2)Cl_4$, crystallises in colourless, four-sided plates, which melt and decompose at 300°; the corresponding *bromide*, $(Cd,C_2H_{10}N_2)Br_4$, occurs in colourless, columnar crystals which decompose about 190°.

Ethylenediammonium uranyl chloride, $(UO_2,C_2H_{10}N_2)Cl_4,2H_2O$, forms yellow, prismatic crystals, which are very hygroscopic and melt about 219°.

Ethylenediammonium ferrous sulphate, $(Fe,C_2H_{10}N_2)(SO_4)_2,4H_2O$, occurs in light green, tabular crystals; *ethylenediammonium cobaltosulphate*, $(Co,C_2H_{10}N_2)(SO_4)_2,4H_2O$, in rose-coloured, triclinic crystals; and *ethylenediammonium manganosulphate*, $(Mn,C_2H_{10}N_2)(SO_4)_2,4H_2O$, in faintly rose-coloured crystals. *Ethylenediammonium nickelosulphate*, $(Ni,C_2H_{10}N_2)(SO_4)_2,6H_2O$, forms green, triclinic crystals; the corresponding *cadmium* compound, $(Cd,C_2H_{10}N_2)(SO_4)_2,4H_2O$, occurs in colourless, triclinic crystals; the *copper* compound,

$$(Cu,C_2H_{10}N_2)(SO_4)_2,6H_2O,$$

in monoclinic crystals; the *zinc* compound, $(Zn,C_2H_{10}N_2)(SO_4)_2,6H_2O$, in colourless, monoclinic crystals; and the *magnesium* compound, $(Mg,C_2H_{10}N_2)(SO_4)_2,4H_2O$, in small, colourless needles. *Ethylenediammonium aluminosulphate*, $(Al_2,C_2H_{10}N_2)(SO_4)_4,4H_2O$, occurs in colourless leaflets. *Ethylenediammonium uranylosulphate*,

$$(UO_2,C_2H_{10}N_2)(SO_4)_2,4H_2O,$$

forms small, light yellow, six-sided crystals, which decompose above 285°; *ethylenediammonium uranylonitrate*, $(UO_2,C_2H_{10}N_2)(NO_3)_4,2H_2O$, forms greenish-yellow, four-sided, columnar crystals, which melt about 215° and are strongly fluorescent. The double uranyl nitrate acts on the photographic plate, whilst the double sulphate and chloride have no action on it; on the other hand, the electroscope is affected about equally by the nitrate and the sulphate. The crystals of the double sulphates described in this paragraph have been measured and the results are tabulated.

Attempts were made to obtain double sulphates containing ethylamine, but only the zinc compound was obtained. *Ethylammonium zinc sulphate*, $(Zn,2C_2H_8N)(SO_4)_2,8H_2O$, obtained by interaction of ethylamine sulphate and zinc sulphate in aqueous solution, occurs in large, colourless crystals. G. S.

Preparation of Aminoalcohols. J. D. Riedel (D.R.-P. 169746, 169819).—The aminoalcohols having the general formula

$$HO{\cdot}CRR^1{\cdot}CH_2{\cdot}NR^2R^3,$$

where R, R^1, R^2, and R^3 are alkyl or aryl groups, are substances which may be employed in the production of anæsthetics. The halogen hydrins required for the preparation of these aminoalcohols are readily obtained from chloroacetone and its analogues by the Grignard reaction. The following carbinols were thus obtained for the first time:

Methylchloromethylpropylcarbinol, $CH_2Cl\cdot CMePr^{\alpha}\cdot OH$, boiling at 75° under 35 mm. pressure; *methylchloromethyl*iso*butylcarbinol*, $CH_2Cl\cdot CMe(C_4H_9)\cdot OH$, boiling at 85° under 25 mm. pressure; *methylchloromethyl*iso*amylcarbinol*, $CH_2Cl\cdot CMe(C_5H_{11})\cdot OH$, boiling at 96—98° under 23 mm. pressure; *benzylmethylchloromethylcarbinol*, $CH_2Cl\cdot CMe(C_7H_7)\cdot OH$, boiling at 155° under 25 mm. pressure; *chloromethyldiethylcarbinol*, $CH_2Cl\cdot CEt_2\cdot OH$, boiling at 88° under 35 mm. pressure.

Dimethylaminomethyldiethylcarbinol, $NMe_2\cdot CH_2\cdot CEt_2\cdot OH$, obtained by the action of dimethylamine on the last of these chlorohydrins at 130°, is a colourless liquid boiling at 76—79° under 23 mm. pressure; the *hydrochloride* of its *benzoyl* derivative crystallises from alcohol in well-defined, lustrous plates melting at 189°.

Dimethylaminodimethylethylcarbinol, $NMe_2\cdot CH_2\cdot CMeEt\cdot OH$, is a colourless liquid boiling at 57° under 23 mm. pressure; the *hydrochloride* of its *benzoyl* derivative melts at 175°.

Dimethylaminodimethylpropylcarbinol, $NMe_2\cdot CH_2\cdot CMePr^{\alpha}\cdot OH$, boils at 78° under 35 mm. pressure; its salts are not crystallisable, but the *hydrochloride* of its *benzoyl* derivative separates in very soluble hygroscopic needles melting at 146°.

*Dimethylaminodimethyl*iso*butylcarbinol* boils at 82° under 34 mm. pressure, the *hydrochloride* of the *benzoyl* derivative melts at 134°.

*Dimethylaminodimethyl*iso*amylcarbinol* boils at 98—99° under 24 mm. pressure; the *hydrochloride* of the *benzoyl* derivative forms silky needles and melts at 138°.

Phenylmethylaminodimethylcarbinol, $NHMe\cdot CH_2\cdot CMePh\cdot OH$, boils at 135—138° under 31 mm. pressure; its *hydrochloride* melts at 153° and its *dibenzoyl* derivative at 122°.

Phenyldimethylaminodimethylcarbinol, $NMe_2\cdot CH_2\cdot CMePh\cdot OH$, boils at 135—136° under 32 mm. pressure; its *hydrochloride* melts at 159—160°.

Phenyldiethylaminodimethylcarbinol, $NEt_2\cdot CH_2\cdot CMePh\cdot OH$, is a viscid liquid boiling at 147—149° under 24 mm. pressure.

Benzyldimethylaminodimethylcarbinol, $NMe_2\cdot CH_2\cdot CMe(C_7H_7)\cdot OH$, boils at 144° under 24 mm. pressure, the *hydrochloride* of its *benzoyl* derivative melts at 195°.

This series of aminoalcohols can also be prepared by applying the Grignard reaction to the dialkyl-aminoacetones and -aminoesters in the following manner:

1. $NMe_2\cdot CH_2\cdot CO\cdot CH_3 \longrightarrow NMe_2\cdot CH_2\cdot CMe_2\cdot O\cdot MgI \longrightarrow NMe_2\cdot CH_2\cdot CMe_2\cdot OH.$
2. $NMe_2\cdot CH_2\cdot CO\cdot OEt \longrightarrow NMe_2\cdot CH_2\cdot CEt_2\cdot O\cdot MgBr \longrightarrow NMe_2\cdot CH_2\cdot CEt_2\cdot OH.$

G. T. M.

Phosphotungstates of some Amino-acids. M. BARBER (*Monatsh.*, 1906, **27**, 379—401. Compare Gulewitsch, Abstr., 1899, i, 833; Schulze and Winterstein, Abstr., 1902, i, 137; Grossmann and Kraemer, Abstr., 1904, i, 850).—*Glycine phosphotungstate*,

$$3C_2H_5O_2N,H_3PO_4,12WO_3,5—6H_2O,$$

which crystallises in stout prisms and nodular aggregates, and is decomposed by boiling alcohol, *alanine phosphotungstate*,

$$3C_3H_7O_2N,H_3PO_4,12WO_3,4—5H_2O,$$

which crystallises in microscopic, stout, pointed needles, *asparagine phosphotungstate*, $5C_4H_8O_3N_2,2H_3PO_4,22WO_3,10H_2O$, and *aspartic acid phosphotungstate*, $4C_4H_7O_4N,2H_3PO_4,20—22WO_3,24H_2O$, which crystallises in microscopic octahedra, are prepared by adding 50 per cent. phosphotungstic acid to the hot saturated aqueous solution of the amino-acid, or by dissolving the latter in the phosphotungstic acid solution, so that the proportion present is 1 amino-acid : 10 phosphotungstic acid. These four phosphotungstates lose their water of crystallisation at 105°. The phosphotungstate of glycine is soluble to the extent of 4·5, 14·4, and 21·3, of alanine to the extent of 15·7, 19·4, and 27·6, of asparagine, 6·8, 66, and 400, and of aspartic acid, 3, 24, and 400, in water, absolute alcohol, and 80 per cent. alcohol, respectively.

Glutamic acid and phosphotungstic acid yield products which have the approximate composition $C_5H_9O_4N,3(H_3PO_4,12WO_3)$, or, after recrystallisation from water, $3C_5H_9O_4N,2(H_3PO_4,12WO_3)$. These are isomorphous mixtures of the phosphotungstate and phosphotungstic acid, and on further recrystallisation from water yield other isomorphous mixtures of varying intermediate composition.

Crystalline phosphotungstates could not be obtained from tyrosine or leucine (compare Kossel and Kutscher, Abstr., 1901, i, 107).

Various methods of separating phosphorus from tungstic acid in organic phosphotungstates are compared. Satisfactory results were obtained only with Sprenger's method (Abstr., 1881, 140) when modified by precipitation of the phosphoric acid by means of ammonium molybdate, instead of ferric chloride and ammonium acetate. G. Y.

Synthesis of Glycocholic and Taurocholic Acids. S. BONDI and ERNST MÜLLER (*Zeit. physiol. Chem.*, 1906, **47**, 499—506).—Pure cholic acid melts at 198° and is most readily prepared by a modification of Mylius' method (Abstr., 1888, 508). The ethyl ester melts at 162°. The *hydrazide*, $C_{23}H_{39}O_3·CO·NH·NH_2$, obtained by heating an alcoholic solution of the ester with hydrazine hydrate, crystallises from hot water in colourless, glistening needles containing water of crystallisation. The anhydrous compound melts at 188—189°, dissolves in most organic solvents, and reduces a cold ammoniacal silver nitrate solution. The solution of the hydrazide in dilute hydrochloric acid yields with benzaldehyde a precipitate of *cholalbenzylidenehydrazine*,

$$C_{23}H_{39}O_3·CO·NH·N:CHPh,$$

The *azide* of cholic acid, $C_{23}H_{39}O_3·CON_3$, obtained by the action of nitrous acid on the hydrazide, is precipitated as a fine powder, decomposes vigorously at 73°, is insoluble in water, but dissolves readily in alcohol or chloroform. The azide condenses with alkaline solutions of glycine and taurine, yielding respectively glyco- and taurocholic acids. J. J. S.

Preparation of Bromodialkylacetamides. KALLE & Co. (D.R.-P. 170629).—Ethyl bromodiethylacetate when dissolved in alcohol and shaken for some time with aqueous ammonia yields bromodiethylacetamide, which can be recrystallised from light petroleum. This amide is also obtained by carefully heating ammonium bromodiethylacetate at 110° under diminished pressure; ammonium bromodipropylacetate can be converted similarly into bromodipropylacetamide. G. T. M.

Acyl Derivatives of Cyanamide and Carbamide. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 167138).—Cyanoacetic acid or the halogenated acetic acids interact readily with cyanamide or its monoalkyl derivatives. Chloroacetylmethylcarbamide results from the interaction of chloroacetic acid and methylcyanamide in ethereal solution.

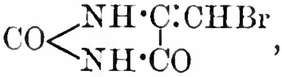
Cyanoacetylmethylcarbamide, $CN\cdot CH_2\cdot CO\cdot NH\cdot CO\cdot NHMe$, obtained in a similar manner from cyanoacetic acid and methylcyanamide, crystallises in colourless needles and melts at 206°. G. T. M.

Action of Bromine on α-Lactylcarbamide and Related Compounds SIEGMUND GABRIEL (*Annalen*, 1906, **348**, 50—90. Compare Abstr., 1905, i, 265; Fischer and Roeder, Abstr., 1902, i, 124; Andreasch, Abstr., 1903, i, 157).—The constitution of pyruvic ureide (Grimaux, this Journal, 1875, 358) is discussed, and

$$CO<\begin{matrix}NH\cdot C{:}CH\cdot CMe\cdot NH\\ NH\cdot CO \quad\quad CO{-}NH\end{matrix}>CO$$

adopted as the most probable.

α-Methylhydantoin (α-lactylcarbamide) yields pyruvic ureide when heated with 1 mol. of bromine in aqueous solution in a sealed tube on the water-bath. When heated with 1 mol. of bromine in glacial acetic acid solution under varying conditions, it yields pyruvic ureide, α-bromomethylenehydantoin, and the *hydrobromide* of pyruvic ureide hydrate, $C_8H_{10}O_5N_4,HBr$; this crystallises in flat, stout, short prisms, sinters at about 205°, and melts and decomposes at 210—211°. When treated with water, it is converted into *pyruvic ureide hydrate*, $C_8H_{10}O_5N_4,2H_2O$, which forms glistening, flat needles, loses $2H_2O$ at 100°, sinters and becomes yellow at 233°, melts and decomposes at 243—244°, and yields pyruvic ureide when heated with concentrated sulphuric acid and diluted with water.



α-Bromomethylenehydantoin, $CO<\begin{matrix}NH\cdot C{:}CHBr\\ NH\cdot CO\end{matrix}$, is formed also by the action of 2 mols. of bromine on α-methylhydantoin in glacial acetic acid solution on the water-bath; it crystallises in slightly yellow needles, melts and decomposes at 241—242°, and is reduced to α-methylhydantoin by fuming hydriodic acid.

The action of 3 mols. of bromine on α-methylhydantoin in glacial acetic acid solution leads to the formation of α-dibromomethylenehydantoin (Fischer, Abstr., 1887, 918), which is formed also by dissolving tribromopyruvylcarbamide (Fischer, *loc. cit.*) in concentrated sulphuric acid, and is reduced to α-methylhydantoin by hydriodic acid.

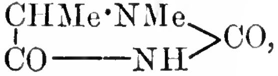
The action of bromine water on α-bromomethylenehydantoin leads to the formation of α-dibromomethylenehydantoic acid,

$$NH_2{\cdot}CO{\cdot}NH{\cdot}C(CO_2H){:}CBr_2,$$

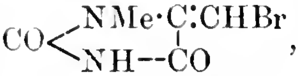
which melts and decomposes at 207° and is identical with Grimaux's dibromodihydromalonylcarbamide (*loc. cit.*), but, contrary to that author's statement, gives a brownish-yellow coloration with dilute ammonia. When heated with concentrated sulphuric acid at 80°, it is converted into α-dibromomethylenehydantoin. The *methyl* ester, $C_5H_6O_3N_2Br_2$, formed by heating the above acid with methyl alcohol and hydrogen chloride, crystallises in flat needles and melts at 208°.

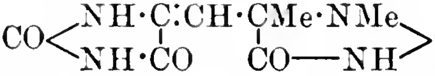
When heated with α-bromomethylenehydantoin and hydrogen bromide in glacial acetic acid solution, α-methylhydantoin forms pyruvic ureide; the condensation does not take place in the absence of hydrogen bromide.

Dihydropyruvic ureide, $C_8H_{10}O_4N_4$, formed with development of heat when pyruvic ureide, or its hydrate, or the hydrobromide of the hydrate is reduced with fuming hydriodic acid, crystallises from boiling water in transparent, flat, pointed, white plates, becomes brown at about 282°, and melts and decomposes at 299°. When hydrolysed with barium hydroxide and water under pressure at 165°, it yields alanine, carbon dioxide, and ammonia; with hydrochloric acid at 165°, it yields ammonia and *dialanine,* $CO_2H{\cdot}CH(NH_2){\cdot}CH_2{\cdot}CMe(NH_2){\cdot}CO_2H$, which crystallises in thin, hexagonal leaflets or needles, melts and decomposes at 248—249°, forms a readily soluble crystalline *hydrochloride* and a *platinichloride,* is converted into dihydropyruvic ureide by the action of potassium cyanate in aqueous solution, and yields 4N when treated with an excess of barium nitrite and dilute sulphuric acid (Fischer and Koelker, Abstr., 1905, i, 692).

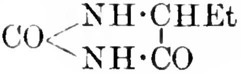
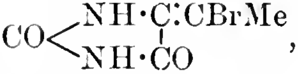
αβ-Dimethylhydantoin,  $\left.\begin{array}{l}\mathrm{CHMe{\cdot}NMe}\\ \mathrm{CO{-\!-\!-\!-}NH}\end{array}\right>\mathrm{CO}$, is prepared by shaking ethyl α-bromopropionate with aqueous methylamine, heating the resulting solution at 100°, evaporating with barium hydroxide, and, after removal of the barium as carbonate, treating the residue with potassium cyanate in aqueous solution. It crystallises in stout, colourless needles, melts at 120—121°, is readily soluble in water, alcohol, ethyl acetate, chloroform, or acetone, less so in ether, and is only sparingly soluble in light petroleum. When treated with 1 mol. of bromine in glacial acetic acid solution, it yields the *hydrobromide* of pyruvic dimethylureide hydrate, $C_8H_8O_5N_4Me_2,HBr$, which crystallises in needles, darkens at 200°, and melts and decomposes at 285°. *Pyruvic dimethylureide hydrate,* $C_8H_8O_5N_4Me_2$, crystallises in colourless, quadratic plates or scales, melts and decomposes at 255—256°, and is reduced by fuming hydriodic acid to *dihydropyruvic dimethylureide,* $C_8H_8O_4N_4Me_2$, which crystallises in colourless leaflets and melts at 275—277°.

The action of 2 mols. of bromine on αβ-dimethylhydantoin in glacial acetic acid solution leads to the formation of *β-methyl-α-bromo-*

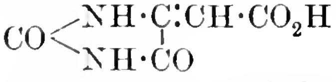
methylenehydantoin,  $\mathrm{CO}<\begin{matrix}\mathrm{NMe\cdot C{:}CHBr}\\ \mathrm{NH{-}{-}CO}\end{matrix}$, which crystallises in pointed, yellow needles, melts at 143—144°, and is readily reduced by hydriodic acid.

a-Bromomethylenehydantoin and *aβ*-dimethylhydantoin interact in presence of hydrogen bromide in glacial acetic acid solution, forming *pyruvic methylureide,*  $\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot C{:}CH\cdot CMe\cdot NMe}\\ \mathrm{NH\cdot CO\quad\ CO{-}{-}NH}\end{matrix}>\mathrm{CO}$, which crystallises in microscopic needles or prisms and melts and decomposes at about 299—300°.

a-Ethyl-lacturamic acid, $\mathrm{NH_2\cdot CO\cdot NEt\cdot CHMe\cdot CO_2H}$, prepared from ethylamine, ethyl a-bromopropionate, and potassium cyanate, forms rhombic crystals, melts and decomposes at 155°, and when evaporated with hydrochloric acid yields a-methyl-*β*-ethylhydantoin (Duvillier, Abstr., 1896, i, 89), which crystallises in rhombic plates and melts at 85°. This condenses with a-bromomethylenehydantoin in presence of hydrogen bromide in glacial acetic acid solution, forming *pyruvic ethylureide,*  $\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot C{:}CH\cdot CMe\cdot NEt}\\ \mathrm{NH\cdot CO\quad\ CO{-}{-}NH}\end{matrix}>\mathrm{CO}$, which crystallises in short, pointed prisms and melts and decomposes at 249°.

a-Ethylhydantoic acid, $\mathrm{NH_2\cdot CO\cdot NH\cdot CHEt\cdot CO_2H}$, prepared from ethyl *a*-bromobutyrate, ammonia, and potassium cyanate, crystallises in quadratic plates and melts and decomposes at 177°. *a-Ethylhydantoin,*  $\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot CHEt}\\ \mathrm{NH\cdot CO}\end{matrix}$, crystallises in leaflets, melts at 117—118°, and on bromination in glacial acetic acid solution yields *a-bromoethylidenehydantoin,*  $\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot C{:}CBrMe}\\ \mathrm{NH\cdot CO}\end{matrix}$, which forms rhombic leaflets and melts and decomposes at 230—236°.

Hydantoin is oxidised by bromine in glacial acetic acid solution, forming parabanic acid. The condensation of hydantoin with a-bromomethylenehydantoin in presence of hydrogen bromide in acetic acid solution leads to the formation of only a small amount of pyruvic ureide.

Malylureide (Guareschi, Abstr., 1878, 138), formed by the action of potassium cyanate on aspartic acid, melts and decomposes at 224—226°, and when treated with bromine in acetic acid solution yields the *acid,*  $\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot C{:}CH\cdot CO_2H}\\ \mathrm{NH\cdot CO}\end{matrix}$, which crystallises in rhombic leaflets, decomposes at 280—350°, forms crystalline *barium* and *silver* salts, is reduced to malylureide by fuming hydriodic acid, and on treatment with bromine water forms *a*-dibromomethylenehydantoic acid. G. Y.

Action of Urethane and of Carbamide on Ethyl Glyoxylate. New Synthesis of Allantoin.

Louis J. Simon and J. Chavanne (*Compt. rend.*, 1906, **143**, 51—54. Compare this vol., i, 396).—*Ethyl diurethaneglyoxylate,* $\mathrm{CH(NH\cdot CO_2Et)_2\cdot CO_2Et}$, obtained by the condensation of ethyl glyoxylate with urethane, crystallises in colourless, transparent prisms, melts at 143°, can be distilled under reduced pressure, dissolves in alcohol, acetic acid, or chloroform, and is stable in boiling water. The *amide*, $CH(NH\cdot CO_2Et)_2\cdot CO\cdot NH_2$, melts at 190° and is soluble in alcohol or hot water; the *acid*,

$$CH(NH\cdot CO_2Et)_2\cdot CO_2H,2H_2O,$$

obtained from the ester by the action of aqueous or alcoholic potassium hydroxide, crystallises from boiling water in thin, silky needles, melts at 159—160°, and loses its water of crystallisation at 110—115°; the anhydrous acid melts at 165°. Diurethaneglyoxylic acid is much more stable than its higher homologue, diurethanepyruvic acid (this vol., i, 404); it is soluble in alcohol, forms crystalline salts with phenylhydrazine or the aromatic bases, reddens litmus, can be titrated in the presence of phenolphthalein, and is precipitated by mineral acids from a solution of its alkali salt.

Ethyl glyoxylate condenses with carbamide in the presence of hydrogen chloride to form *ethyl allantoate*, $CH(NH\cdot CO\cdot NH_2)_2\cdot CO_2Et$, a white, microcrystalline substance which decomposes at 200°. It is converted into allantoin by the action of ammonia or alkali hydroxides, and in this respect resembles its higher homologue, ethyl homoallantoate (Abstr., 1902, i, 15; 1904, i, 300), from which, however, it differs in its stability towards boiling water, which decomposes ethyl homoallantoate, whilst ethyl allantoate can be recrystallised from that solvent or from boiling alcohol; it is decomposed by acids, regenerating ethyl glyoxylate. M. A. W.

Preparation of Aminoguanidine from Nitroguanidine. C. F. BOEHRINGER & SÖHNE (D.R.-P. 167637).—The electrolytic reduction of nitroguanidine with zinc and platinum electrodes gives unsatisfactory results, but when either a tin cathode is used or a tin salt or finely-divided tin is added to the solution, the yield of aminoguanidine is greatly increased. The nitro-compound is suspended in water slightly acidified with sulphuric acid. A tin cathode with roughened surface is employed and the current density is 250 amperes per sq. metre; the temperature is maintained at 10°, and during the electrolysis just sufficient acid is added from time to time to fix the amine which is being produced; the yield is 81 per cent. of the theoretical. G. T. M.

Substances extracted from Muscle. III. Methylguanidine. WLADIMIR GULEWITSCH (*Zeit. physiol. Chem.*, 1906, **47**, 471—475. Compare Abstr., 1900, i, 516; 1905, i, 726; also Kutscher, *Zeit. Nahr. Genussm.*, 1905, **10**, 531).—Methylguanidine has been isolated from the extract of muscle. The nitrate of the base melts at 150°. The *picrate*, whether obtained from creatine or from muscle extract, crystallises from water in two distinct modifications: a yellow form crystallising in four- or six-sided pleochroic plates, and an orange-coloured form crystallising in short, four-cornered plates also showing pleochroism. When crystallised under certain conditions, each form can be partially transformed into the other. Guanidine picrate also crystallises in two distinct forms (von Cordier, this vol., i, 486). J. J. S.

Action of Sulphides on Nitroprussides. JUAN F. VIRGILI (*Zeit. anal. Chem.*, 1906, **45**, 409—439. Compare Abstr., 1902, ii, 472).—An attempt is made to explain the different colours produced on mixing solutions of sodium nitroprusside with soluble sulphides.

The reddish-yellow, red, purple, and violet shades which are obtained under different conditions are due to the simultaneous formation of two substances, one of which is blue and represents a molecular compound of the sulphide and the nitroprusside, whilst the other (a quaternary nitroprusside) is yellow and is formed by the action of alkali hydroxide on the normal nitroprusside. This view is supported by a study of the absorption spectra. In order to obtain the blue coloration, free alkali hydroxide and alkali salts of weak acids must be absent. It is readily produced when the nitroprusside is added to an excess of a concentrated solution of the sulphide in ethyl alcohol or glycerol, or to an aqueous solution containing excess of hydrogen sulphide. On account of the increasing hydrolysis, a larger excess of hydrogen sulphide is required with increasing dilution, and by reason of the weak basic character of ammonia the blue coloration is more readily obtained with ammonium sulphide than with the alkali metal sulphides. With solutions of the alkali hydrogen sulphides, the colour is distinctly more blue than with corresponding solutions of the normal sulphides. These facts are readily explained by the author's hypothesis.

Experiments on the mixing of solutions under different conditions indicate that the nitroprusside does not react with the sulphide ion but with the non-ionised sulphide. The intensity of the coloration increases when salts with a common ion are added to the solution or when solvents of smaller ionising power are used. The sensitiveness of the nitroprusside as a reagent for sulphide is considerably diminished in consequence of hydrolysis, and addition of substances which decrease the hydrolysis (alkali hydroxides) increases the sensitiveness. Low temperature also increases the sensitiveness; whilst at 20° sodium sulphide could be detected at a concentration of 0·0033 gram per litre, it was found that at 0° the colour change was given at a concentration of 0·0011 gram per litre. On account of the difficulty of obtaining comparable colorations, nitroprusside is not suitable for the estimation of hydrogen sulphide. H. M. D.

Attempts to Synthesise Phenylallene. AUGUST KLAGES and KARL KLENK (*Ber.*, 1906, **39**, 2552—2555).—Cinnamyl chloride, obtained from cinnamyl alcohol and hydrogen chloride in the cold, boils at 120° under 18 mm. pressure, has a sp. gr. 1·101 at 15°/4°, and, contrary to statements in the literature, forms a *dibromide* which melts at 104—105°. When heated with pyridine (2 mols.), it yields a *pyridinium chloride*, which is easily soluble in water and alcohol, and forms a yellow platinichloride and aurichloride, and a white mercurichloride.

Cinnamyl bromide, C_9H_9Br, obtained from cinnamyl alcohol and hydrogen bromide in glacial acetic acid at 0°, melts at 34°, boils at 103° under 22 mm. pressure, forms with bromine long, white needles of $\alpha\beta\gamma$-tribromo-α-phenylpropane, which melts at 128°, and is converted by alcoholic potash at 130° into *cinnamyl ethyl ether*,

$$CHPh{:}CH{\cdot}CH_2{\cdot}OEt,$$

a colourless oil which boils at 231—232°.

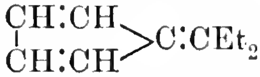
The reaction between magnesium phenyl bromide and acraldehyde leads to the formation of *α-phenylallyl alcohol*, $OH{\cdot}CHPh{\cdot}CH{:}CH_2$, an oil which boils at 106° under 18 mm. and at 214° under 746 mm. pressure, has a sweet burning taste, and yields with excess of bromine the tribromide previously described. *a-Phenylallyl chloride*,

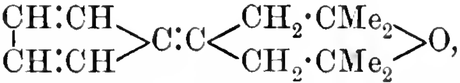
$CHPhCl\cdot CH{:}CH_2$,

is a colourless oil with a strong odour; with bromine it forms an additive *compound*, $C_9H_9ClBr_2$, which melts at 104°.

a-Phenylallyl bromide is a colourless oil with an irritating vapour; it solidifies in ice and is converted by alcoholic potash at 120° into *a-phenylallyl ethyl ether*, $CH_2{:}CH\cdot CHPh\cdot OEt$, an oil which has a faint fruity odour and boils at 203—205° under 755 mm. pressure. C. S.

Condensation Products of *cyclo*Pentadiene. JOHANNES THIELE and HANS BALHORN [in part with WALTHER ALBRECHT] (*Annalen*, 1906, **348**, 1—15. Compare Thiele, Abstr., 1900, i, 298; this vol., i, 569, 586).—Methylethylfulvene (Engler and Frankenstein, Abstr., 1901, i, 658), prepared by the condensation of *cyclo*pentadiene with methyl ethyl ketone in presence of sodium ethoxide in cooled alcoholic solution, boils at 62·5° under 13 mm. pressure, volatilises with ether vapour, gives a red coloration and a light precipitate with glacial acetic-sulphuric acid, and resinifies when exposed to air.

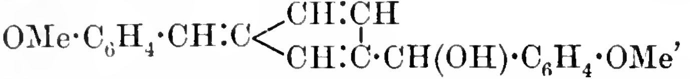
Diethylfulvene,  $\begin{matrix}CH{:}CH\\ |\\ CH{:}CH\end{matrix}\!\!>C{:}CEt_2$, prepared in the same manner from *cyclo*pentadiene and diethyl ketone, boils at 74·5—78·5° under 19 mm. pressure and closely resembles dimethylfulvene in its colour, odour, and reactions.

A *product*,  $\begin{matrix}CH{:}CH\\ |\\ CH{:}CH\end{matrix}\!\!>C{:}C\!<\!\begin{matrix}CH_2\cdot CMe_2\\ CH_2\cdot CMe_2\end{matrix}\!\!>O$, is formed together with dimethylfulvene by the condensation of acetone with *cyclo*pentadiene in alcoholic sodium ethoxide or concentrated methyl-alcoholic potassium hydroxide solution, or with dimethylfulvene in presence of alcoholic sodium ethoxide; it is obtained as a dark orange oil which boils at 110° under 11 mm. pressure.

Freshly-distilled dimethylfulvene solidifies quickly when cooled with ice, forming yellow crystals melting at about 4°, but after four to five months the oil solidifies only slowly and the yellow crystals change at the ordinary temperature into *bisdimethylfulvene*, $C_{16}H_{20}$, which crystallises from alcohol in hexagonal plates or needles, melts at 83°, yields dimethylfulvene when heated above its melting point, is not resinified by air, gives a yellowish-red coloration with concentrated sulphuric acid, reduces potassium permanganate immediately in alcoholic solution, and forms an *additive* compound with 2 mols. of bromine. iso*Nitrosodimethylfulvene*, $C_5H_4{:}CMe\cdot CH{:}NOH$, prepared from *iso*nitrosoacetone and *cyclo*pentadiene, crystallises in glistening, reddish-brown needles or prisms, melts at 87°, has a characteristic odour, reduces ammoniacal silver and Fehling's solutions when heated, and is dissolved and decomposed by warm dilute sulphuric acid.

*Cinnamylidene*cyclo*pentene*, $C_5H_4{:}CH\cdot CH{:}CHPh$, formed by condensation of *cyclo*pentadiene and cinnamaldehyde in presence of methyl-alcoholic potassium hydroxide, crystallises in bluish-red needles, melts at 102°, is rapidly oxidised by moist oxygen, gives a violet to blue coloration with concentrated sulphuric acid, forms an *additive* compound with bromine, and is reduced by aluminium amalgam to an *oil* which readily resinifies.

The condensation of *cyclo*pentadiene with anisaldehyde leads to the formation of *p*-methoxyphenylfulvene and p-*methoxyphenyl-a-hydroxy-*p-*methoxybenzylfulvene,*



$$OMe\cdot C_6H_4\cdot CH{:}C\Big\langle\begin{matrix}CH{:}CH \\ CH{:}C\cdot CH(OH)\cdot C_6H_4\cdot OMe\end{matrix},$$

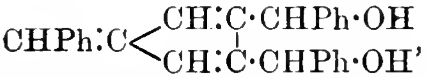
which crystallises in sheaves of red prisms, melts at 129°, is readily oxidised, and with concentrated sulphuric acid gives a deep blue coloration becoming red.

p-*Methoxyphenylfulvene,* $C_5H_4{:}CH\cdot C_6H_4\cdot OMe$, crystallises in short, red spears, melts at 70°, and gives an orange coloration with concentrated sulphuric acid.

p-*Methoxybenzyl*cyclo*pentene,* $C_5H_5\cdot CH_2\cdot C_6H_4\cdot OMe$, formed by reduction of the last substance with aluminium amalgam in moist ether, is obtained as a light orange oil, which on cooling deposits a small amount of white crystals melting at 163°. The oil boils at 153—154° under 9 mm. pressure, and solidifies to glistening, colourless crystals melting at 53°. It forms an *additive* compound with bromine, and gives an orange coloration with concentrated sulphuric acid.

The yellow, insoluble condensation product of *cyclo*pentadiene with formaldehyde contains a polymeride of fulvene together with oxygen compounds.

Phenyldi-a-hydroxybenzylfulvene,



$$CHPh{:}C\Big\langle\begin{matrix}CH{:}C\cdot CHPh\cdot OH \\ CH{:}C\cdot CHPh\cdot OH\end{matrix},$$

formed by the condensation of *cyclo*pentadiene with benzaldehyde, crystallises in red needles, melts at 178—179°, absorbs bromine, and gives a violet coloration with concentrated sulphuric acid.

Diphenylfulvene dibromide, $C_{18}H_{14}Br_2$, crystallises in yellow plates, melts at 102—102·5°, and decomposes on exposure to air. The *tetrabromide,* $C_{18}H_{14}Br_4$, forms yellow plates, melts at 123°, dissolves in boiling aniline, alcohol, or glacial acetic acid, forming red solutions, gives a green coloration when reduced with zinc dust in chloroform or benzene, is decomposed by alcoholic alkali hydroxides, and forms silver bromide when heated with silver nitrate solution. The *diacetate,*

$$C_{18}H_{14}Br_2(OAc)_2,$$

formed by boiling the tetrabromide with potassium acetate in glacial acetic acid solution, crystallises in white leaflets and melts at 166—167°.

G. Y.

So-called Aromatic Substances containing Six Atoms of Carbon. Georg Körner (*Atti R. Accad. Lincei,* 1906, [v], **15**, i, 525—526).—In the chemistry of the halogen- and nitro-substitution products of benzene there are still many gaps, besides which many incorrect data have been published. The author proposes to fill up the gaps in, and revise generally, the knowledge of the formation and properties of aromatic compounds containing six carbon atoms, with a view to ascertaining the influence of the nature and position of each substituent atom or group of atoms on the ultimate properties of the molecule (compare following abstract).

T. H. P.

The Sixth Dibromonitrobenzene. GEORG KÖRNER and ANGELO CONTARDI (*Atti R. Accad. Lincei*, 1906, [v], **15**, i, 526—528).—On treating *o*-dibromobenzene with nitric acid of sp. gr. 1·54, adding concentrated nitric acid, and subsequently pouring the product of the reaction into water, a mixture of 3 : 4-dibromo-1-nitrobenzene and 2 : 3-dibromo-1-nitrobenzene is obtained. By extracting with 95 per cent. alcohol and cooling the solution, the former is separated and, after a single crystallisation, melts at 57—58°.

Concentration of the alcoholic mother liquors yields a crystalline mixture melting at 42° and, on treating this with acetic acid, 2 : 3-*dibromo*-1-*nitrobenzene* is obtained; it crystallises from acetic acid or ethyl acetate in thick, monoclinic prisms [E. REPOSSI: $a:b:c = 1{\cdot}031:1:0{\cdot}282$; $\beta = 80^\circ 8' 30''$], melts at 85·2° and dissolves readily in acetone or chloroform, and to a less extent in ether; on replacing the nitro-group by an amino-residue and the latter by a bromine atom, 1 : 2 : 3-tribromobenzene, melting at 87·4°, is obtained; when treated with alcoholic ammonia solution at 180°, 2 : 3-dibromo-1-nitrobenzene yields 2-*bromo*-6-*nitroaniline*, which crystallises in pale yellow needles melting at 73·4°, dissolves moderately easily in alcohol, volatilises readily in a current of steam, and is converted by the action of ethyl nitrite into *m*-bromonitrobenzene. When acted on by a mixture of concentrated sulphuric acid and nitric acid of sp. gr. 1·54, 2 : 3-dibromo-1-nitrobenzene gives a mixture of three dinitro-derivatives.

2 : 3-*Dibromoaniline*, prepared by the action of a hydrochloric acid solution of stannous chloride (3 mols.) on 2 : 3-dibromo-1-nitrobenzene, crystallises from aqueous alcohol in colourless, transparent plates melting at 43°, dissolves readily in alcohol, ether, or ethyl acetate, distils easily in a current of steam, and is a less energetic base than the other *o*-dibromoaniline.

2 : 3-*Dibromoacetanilide*, prepared by boiling 2 : 3-dibromoaniline with acetic anhydride, is slightly soluble in alcohol, from which it separates in acicular crystals melting at 164°.

3-*Bromo*-2-*iodo*-1-*nitrobenzene*, prepared from the bromonitroaniline melting at 73·4° by replacing the amino-group by an iodine atom, forms faintly green, transparent, monoclinic prisms [E. REPOSSI: $a:b:c = 0{\cdot}634:1:0{\cdot}568$; $\beta = 74{\cdot}56^\circ$], melting at 119—120°.

2-*Chloro*-3-*bromo*-1-*nitrobenzene* crystallises from alcohol or ether in green, flattened needles melting at 65°. T. H. P.

New Case of Form-analogy and Miscibility of Position-isomeric Benzene Derivatives and the Crystalline Forms of the Six Dibromonitrobenzenes. FRANS M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, **9**, 26—33).—2 : 3-Dibromo-1-nitrobenzene crystallises in small, flat, sherry-coloured needles belonging to the triclinic system [$a:b:c = 1{\cdot}4778:1:1{\cdot}9513$; $\alpha = 90^\circ 45\frac{2}{3}'$, $\beta = 110^\circ 36\frac{3}{4}'$, $\gamma = 89^\circ 59\frac{1}{4}'$]; the crystals show a decided approach to the monoclinic system. 2 : 5-Dibromo-1-nitrobenzene forms small, pale yellow, lustrous, flattened, triclinic plates [$a:b:c = 1{\cdot}4909:1:2{\cdot}0214$; $\alpha = 90^\circ 57\frac{1}{2}'$, $\beta = 113^\circ 21\frac{1}{3}'$, $\gamma = 90^\circ 2'$]. The two compounds, although closely related, are not isomorphous, but can form an interrupted series of mixed crystals. The binary melting-point curve possesses a eutectic point at 52° with two per cent. of the compound with higher melting point. The mixed crystals contain up to 48 per cent. of the 1 : 2 : 3-derivative and melt between 75° and 84·5°.

The 2 : 4-dibromo-1-nitrobenzene also crystallises in the triclinic system [$a : b : c = 1{\cdot}1307 : 1 : 1{\cdot}1698$; $\alpha = 97°36'$, $\beta = 113°37'$, $\gamma = 87°33'$], but does not form mixed crystals.

The 2 : 6 : 1-, 3 : 5 : 1-, and 3 : 4 : 1-derivatives belong to the monoclinic system. They do not form mixed crystals in binary mixtures, the lower melting point being lowered on addition of the component melting at the higher temperature. The differences in the crystalline forms of the brominated derivatives are much less than those between the corresponding chlorinated compounds. E. F. A.

Preparation of 1 : 2-Dichloro-4-nitrobenzene. K. OEHLER (D.R.-P. 167297).—Polyhalogenated nitro-derivatives of aromatic hydrocarbons are generally obtained by nitrating the halogen compounds; the converse operation, the chlorination of the nitro-compound, has not been successfully performed on a technical scale. One part of anhydrous ferric chloride was added to 20 parts of fused *p*-nitrochlorobenzene and chlorine introduced at 95—110°, until the additional weight of the mixture corresponded with 4·5 parts; the mixture was added to water, when a theoretical yield of 1 : 2-dichloro-4-nitrobenzene was obtained, which, after one crystallisation, gave the correct melting point (43°). The ferric chloride may be replaced by other chlorine carriers, such as iron, phosphorus, antimony pentachloride, or iodine.

G. T. M.

Crystallographic Characters of some Organic Compounds. FRANS M. JAEGER (*Zeit. Kryst. Min.*, 1906, **42**, 158—169).—Crystallographic determinations are given of the following compounds: *o*-nitrobenzyl-*o*-toluidine, diphenylhydrazine, 2 : 4 : 6-trinitro-*m*-xylene, 4 : 5 : 6-trinitro-*m*-xylene, 2 : 5 : 6-trinitro-*m*-xylene, 2 : 3 : 5-trinitro-*p*-xylene, 1 : 2-dichloro-3-nitrobenzene, 1 : 3-dichloro-2-nitrobenzene, 1 : 3-dichloro-5-nitrobenzene, and 1 : 4-dichloro-2-nitrobenzene. L. J. S.

Reduction of Aromatic *o*- and *p*-Dinitro-compounds. JAKOB MEISENHEIMER and EGBERT PATZIG (*Ber.*, 1906, **39**, 2526—2532. Compare Meisenheimer, Abstr., 1904, i, 150).—The *sodium* salt, $C_6H_4O_4N_2Na_2$, formed by reduction of *p*-dinitrobenzene by means of hydroxylamine hydrochloride and sodium methoxide in methyl-alcoholic solution, separates almost quantitatively as a red, crystalline powder, detonates slightly when heated, and dissolves and decomposes in aqueous sodium hydroxide.

The volume of nitrogen evolved on reduction of *o*-dinitrobenzene by hydroxylamine in methyl-alcoholic sodium hydroxide solution agrees with that required by the equation $C_6H_4(NO_2)_2 + 2NH_2{\cdot}OH + 2KOH = C_6H_4(NO_2K)_2 + 4H_2O + N_2$. The *sodium* salt, $C_6H_4O_4N_2Na_2$, is obtained as a red, amorphous powder if the reduction takes place in benzene-methyl-alcoholic solution; it dissolves in water or alcohol, forming a dark blue solution, and when treated with bromine in dilute solution at 0° yields *o*-nitronitrosobenzene as a light yellow precipitate. On passage of a current of carbon dioxide, the blue methyl-alcoholic solution of the sodium salt becomes red and sodium hydrogen carbonate is deposited, the blue solution being again formed on heating. If the solution is diluted with water and saturated with carbon dioxide, *o*-dinitrobenzene is formed slowly.

o-*Nitronitroso*-p-*xylene*, $C_8H_8O_3N_2$, is prepared by reducing the mixture of *o*- and *m*-dinitro-*p*-xylene obtained by the direct nitration of *p*-xylene (Jannasch and Stuenkel, Abstr., 1881, 808) with hydroxylamine hydrochloride in methyl-alcoholic potassium hydroxide solution, extracting the unchanged *m*-dinitro-compound with ether, and adding hydrochloric acid to the cooled solution; it forms slightly yellow crystals, melts at 130·5°, dissolves in hot benzene, chloroform, or glacial acetic acid to green, in alcoholic alkali hydroxides to red solutions, and does not form a condensation product with aniline in glacial acetic acid solution. G. Y.

Phenylnitrolic Acid. HEINRICH WIELAND and LEOPOLD SEMPER (*Ber.*, 1906, **39**, 2522—2526).—*Phenylnitrolic acid*, $NO_2{\cdot}CPh{:}NOH$, is prepared by the successive action of sodium nitrite and oxalic acid on potassium phenylnitromethane in aqueous solution at −15°; it crystallises from light petroleum in slender, colourless needles, has a bitter flavour, melts at 57—58°, and decomposes when heated a few degrees above its melting point or more slowly in alkaline solution, forming nitrous acid and benzonitrile oxide (Werner and Buss, Abstr., 1894, i, 585), which rapidly polymerises to diphenylglyoxime peroxide. This crystallises in glistening, colourless leaflets, melts and decomposes at 114—116° (105°, Beckmann, Abstr., 1889, 980), and gives Liebermann's nitroso-reaction.

When oxidised carefully with potassium permanganate in alkaline solution, phenylnitrolic acid yields benzenylnitrosolic acid (this vol., i, 412). G. Y.

Behaviour of Sulphonic Acids on Oxidation by Fusion. CARL GRAEBE and HERMANN KRAFT (*Ber.*, 1906, **39**, 2507—2512. Compare this vol., i, 255).—When fused with lead peroxide and potassium hydroxide, sulphonic acids are oxidised to the following products, the yields being given in percentages of the theoretical.

p-Toluenesulphonic acid: benzoic acid (78 per cent.) and *p*-hydroxybenzoic acid (2—3 per cent.). *p*-Toluenesulphonamide, 8 per cent. of which remains unchanged: benzoic acid (26·6 per cent.) and *p*-hydroxybenzoic acid (34·7 per cent.). *o*-Toluenesulphonic acid: benzoic acid and *o*-cresol. *o*-Toluenesulphonamide: benzoic acid, *o*-cresol, salicylic acid, and traces of an acid insoluble in chloroform. *o*-Xylene-4-sulphonic acid: phthalic acid (70·5 per cent.). *m*-Xylene-4-sulphonic acid is oxidised only with difficulty: *iso*phthalic acid (33 per cent.) and traces of benzoic and *m*-toluic acids. *p*-Xylenesulphonic acid: terephthalic acid (11 per cent.), *p*-xylenol (26—28 per cent.), and traces of hydroxyterephthalic or salicylic acid. Mesitylenesulphonic acid: trimesic acid (55 per cent.) containing uvitic acid. *p*-Ethylbenzenesulphonic acid: benzoic acid (10 per cent.) and *p*-hydroxybenzoic acid (15 per cent.). *m*-Sulphobenzoic acid: *m*-hydroxybenzoic acid (97 per cent.).

When boiled with aqueous potassium hydroxide and then fused with an anhydrous alkali hydroxide, *o*-tolylsulphone yields benzoic acid (93 per cent.) and a small quantity of an oil having an odour of cresol.

When fused directly with potassium hydroxide, *o*-tolylsulphone is oxidised to benzoic acid and *o*-cresol, the fused mass smelling of benzaldehyde.

When fused with potassium hydroxide, benzaldehyde-4-sulphonic acid yields benzoic (40 per cent.) and *p*-hydroxybenzoic (54 per cent.) acids, benzaldehyde-2-sulphonic acid yields *o*-cresol and benzoic (36·5 per cent.) and salicylic (52 per cent.) acids, whilst *o*-sulphobenzoic acid yields salicylic acid quantitatively. G. Y.

Combination of Mercuric Iodide with Free Amines. Maurice François (*J. Pharm. Chim.*, 1906, [vi], **24**, 21—24).—A general consideration of facts already recorded (this vol., i, 484). Mercuric iodide combines not only with methylamine (*loc. cit.*), but also with aromatic bases; with aniline the *compound* $2NH_2Ph,HgI_2$ is obtained, and with pyridine the *compound* $2C_5NH_5,HgI_2$. The interaction is best effected by warming an alcoholic solution of the base with mercuric iodide; the salt separates in crystals on cooling. The compounds are also formed as a crystalline precipitate by the action of an aqueous solution of the base on a concentrated solution of potassium iodide saturated with mercuric iodide. W. A. D.

Action of Bromine on Aromatic Amines. Substitution Products and Perbromides. Karl Fries (*Annalen*, 1906, **346**, 128—219. Compare Abstr., 1904, i, 571).—On bromination, aromatic amines yield at the ordinary temperature either substitution products or perbromides according to the conditions. The presence of acid is unfavourable to the introduction of bromine into the nucleus. Additive products, perbromides, are produced in the presence of hydrogen halides before substitution takes place, and are converted readily into the substitution products. Perbromides of six types have been observed, X_2Br, XBr, X_2Br_3, XBr_2, XBr_4, and XBr_6, where X represents the hydrobromide of a base. Hydrochlorides form perbromides of the types XBr and XBr_2. Hydriodides form perbromides most, and hydrochlorides least, readily. The salts of quaternary bases show the greatest tendency to form perbromides, and the primary amines the least; but the number and nature of the substituting groups exercise a very great influence. The perbromides of unsubstituted bases are very unstable; they can only be obtained by adding bromine at a low temperature to the hydrobromide of the base suspended in hydrobromic acid. Partially substituted amines, on the other hand, yield well-crystallised stable perbromides. The perbromides give up bromine to all substances reacting with bromine, and in the presence of solvents are generally converted into substitution products, when this is possible. Most dry perbromides give up bromine to the air, the higher bromides passing over into the lower perbromides, some of which (those derived from quaternary salts) are stable under these conditions. All perbromides are decomposed by water. When substitution is not possible, oxidation takes place. The perbromides of secondary and tertiary amines lose, with water, an alkyl group, primary or secondary amines being produced. 2 : 4-Disubstituted tertiary amines behave similarly, but here substitution also takes place, thus: $C_6H_3X_2·NMe_2,HBr,Br_2 = C_6H_2X_2Br·NHMe,HBr + BrMe$.

The diperbromide of *p*-bromodimethylaniline hydrobromide behaves in a unique manner; it yields *p*-bromodimethylaniline, 2 : 4-dibromodimethylaniline, and the perbromide of diphenoquinonetetramethyldiiminium dibromide, $Br_2,NMe_2Br:C_6H_4:C_6H_4:NMe_2Br,Br_2$, which can also be obtained directly by the action of bromine on *p*-bromodimethylaniline.

All the perbromides are similarly constituted, a complex negative ion being present.

The perbromides of all quaternary and many tertiary amines cannot be converted into substitution products, a fact which is in agreement with the direct bromination of aromatic amines. With one mol. of bromine, aniline yields a mixture of mono-, di-, and tri-bromoanilines; methylaniline yields a mixture of mono- and di-bromomethylanilines, and dimethylaniline yields quantitatively bromodimethylaniline. With 2 mols. of bromine, aniline gives the same mixture, monomethylaniline exclusively a dibromo-derivative, and dimethylaniline, dibromodimethylaniline, but with difficulty. Three mols. of bromine convert aniline and methylaniline into the tribromo-derivatives, but transform dimethylaniline into tribromomethylaniline, a methyl group being eliminated. Similar changes are observed if bromine acts on an amine in which a hydrogen atom in the ortho- or the para-positions is already replaced. An alkyl group appears to protect one of the ortho-hydrogen atoms, whilst two alkyl groups prevent both the ortho-hydrogen atoms from being replaced.

The influence of a bromine atom in the ortho-position relatively to the amino-group on the introduction of alkyl groups has also been investigated. All halogenated amines are less readily alkylated than unsubstituted amines; if the halogen is in the ortho-position with respect to the amino-group, the reaction is still further retarded. Thus, excess of methyl iodide and sodium carbonate alkylated, in thirty hours, 30 per cent. of 2 : 4-dibromoaniline, 15 per cent. of 3 : 5-dibromo-*p*-toluidine, and 0 per cent. of *s*-tribromoaniline. Similarly, in the addition of methyl iodide to a tertiary base, it was found that *p*-bromodimethylaniline yielded thirty times as much quaternary iodide as *o*-bromodimethylaniline. Diortho-substituted bases cannot be converted into quaternary bases. It cannot be concluded with certainty that these facts are accounted for by steric hindrance of the reactions.

Large excess of strong acids prevents substitution. Since quaternary salts are also incapable of being substituted, it is argued that the first step in the process of substitution of amines is an addition of the substituting agent to the nitrogen atom.

The *perbromide*, NH_2Ph,HBr,Br_2, is prepared by adding a mixture of bromine and concentrated hydrobromic acid to a mixture of aniline, acetic acid, and hydrobromic acid; it forms yellow crystals, which are reconverted into aniline by treatment with sodium hydrogen sulphite; treated with water or other solvents or on exposure to the air, bromoanilines are formed. *s*-Tribromoaniline yields the *perbromide*, $C_6H_2Br_3\cdot NH_2,HBr,Br_2$, when bromine is added to its solution in acetic acid; it crystallises in garnet-red prisms melting and decomposing at 105°; the fused mass resolidifies and again melts at 205°; all the bromine is eliminated by treatment with solvents or keeping in the air. 3 : 5-Dibromo-*o*-toluidine gives under the same conditions the *perbromide*, $C_6H_2MeBr_2\cdot NH_2,HBr,Br_2$, which forms dark red prisms, losing bromine at 120° and melting at 240°. The corresponding *derivative* of dibromo-*p*-toluidine crystallises in brownish-red plates, which lose bromine at 110° and melt at 225°. *Diacetyl-5-bromo-*1 : 3 : 4-*xylidine,* prepared by prolonged boiling of 5-bromo-*m*-xylidine with acetic anhydride, crystallises in prisms melting at 59°. 6-Bromo-1 : 3 : 4-xylidine is the chief product of the bromination of *m*-xylidine in concentrated sulphuric acid; its *diacetyl* derivative crystallises in plates melting at 70°. 5 : 6-*Dibromo*-1 : 3 : 4-*xylidine,* $C_6HMe_2Br_2\cdot NH_2$, is better prepared from 6-bromo- than from 5-bromo-*m*-xylidine; it crystallises in needles melting at 40°. Its *monoacetyl* derivative crystallises in needles melting at 192°, and its *diacetyl* derivative in prisms melting at 183°. *m*-Xylidine in hydrobromic acid yields the *perbromide*, $C_6H_3Me_2\cdot NH_2,HBr,Br_2$ (?), which appears to be identical with the compound mistaken by Fischer and Windaus (Abstr., 1900, i, 484) for a bromoamine; it crystallises in yellow needles, which readily lose bromine, and is converted by contact with solvents into bromoxylidine. The *perbromide*, $C_6H_2Me_2Br\cdot NH_2,HBr,Br_2$, obtained from 5-bromoxylidine, crystallises in plates melting at 134°.

When acetanilide is treated with 1 mol. of bromine in glacial acetic acid, a *perbromide* of *p*-bromoacetanilide,

$$(C_6H_4Br\cdot NHAc)_2HBr,Br_2,$$

is obtained as yellow plates melting at 135°; on addition of water during the bromination the perbromide is decomposed, *p*-bromoacetanilide alone being formed. In order to form 2 : 4-dibromoacetanilide, dilute acetic acid should be used and sodium acetate added. *s*-Tribromoacetanilide can only be obtained in a yield of 15 per cent. when acetanilide is brominated.

When 1 : 3 : 4-acetxylidide is brominated, besides the 6-bromo-derivative both the 5- and the 2-bromo-derivatives are produced.

2 : 4-*Dibromomethylaniline,* $C_6H_3Br_2,NHMe$, prepared by brominating methylaniline in acetic acid and then cautiously adding water, crystallises in leaflets melting at 48°. 2 : 4 : 6-*Tribromomethylaniline,* prepared similarly, crystallises in needles melting at 39°, boils at 310°, and forms a very sparingly soluble hydrochloride and hydrobromide; the *platinichloride* crystallises in orange plates decomposing at 232°, and the *acetyl* derivative in plates melting at 101°. The *perbromide* of dibromomethylaniline, $(C_6H_3Br_2\cdot NHMe,HBr)_2,Br_2$, is prepared either from dibromomethylaniline or from bromomethylaniline in the presence of hydrobromic acid, and crystallises in yellowish-red prisms melting at 125°; it is converted into tribromomethylaniline by treatment with water. The *perbromide,*

$$(C_6H_3Br_2\cdot NHMe,HCl)_2,Br_2,$$

crystallises in prisms, becoming colourless at 100° and melting at 190°. The *perbromide* from tribromomethylaniline, $C_6H_2Br_3\cdot NHMe,HBr,Br_2$, crystallises in brownish-red needles melting at about 160°; addition of water to its solution in acetic acid converts it into tribromoaniline. The *perbromide,* $C_6H_2Br_3\cdot NHMe,HCl,Br_2$, forms yellowish-red plates which melt at 150° and change in the air into the hydrochloride of *s*-tribromomethylaniline, which crystallises in prisms decomposing at 190°; water converts this perbromide into *s*-tribromoaniline.

5-*Bromomethyl*-o-*toluidine*, $C_6H_3MeBr\cdot NHMe$, prepared from methyl-*o*-toluidine, is an oil boiling at 165° under 25 mm. pressure; the corresponding 3 : 5-*dibromo*-compound boils at 187° under 50 mm. pressure, and yields a *hydrobromide* which darkens at 180° and melts at 220°. The *perbromide*, $C_6H_3MeBr\cdot NHMe,HBr,Br_2$, prepared directly from methyl-*o*-toluidine, crystallises in red prisms decomposing at 105°, and is converted by warming with solvents into dibromotoluidine. The *perbromide*, $C_6H_2MeBr_2\cdot NHMe,HBr,Br_2$, obtained from 3 : 5-dibromomethyltoluidine, crystallises in prisms melting at 142° and is converted by water into 3 : 5-dibromo-*o*-toluidine.

p-*Bromoethylaniline*, $C_6H_4Br\cdot NHEt$, prepared from ethylaniline, melts at 12°; 2 : 4-*dibromoethylaniline* crystallises in plates melting at 51°; 2 : 4 : 6-*tribromoethylaniline*, prepared directly from ethylaniline, crystallises in needles melting at 45°. The *perbromide*, $C_6H_3Br_2\cdot NHEt,HBr,Br_2$, prepared from 2 : 4-dibromoethylaniline in the presence of hydrobromic acid, crystallises in yellowish-red plates melting at 85°, and when warmed with acetic acid passes into tribromoethylaniline. The *perbromide*, $C_6H_2Br_3\cdot NHEt,HBr,Br_2$, crystallises in yellowish-brown prisms melting at 125°, and when heated with dilute acetic acid is converted into tribromoaniline.

3-*Bromoethyl*-p-*toluidine*, $C_6H_3MeBr\cdot NHEt$, is an oil boiling at 143° under 25 mm. pressure; its *hydrobromide* crystallises in prisms decomposing at about 160°. 3 : 5-*Dibromoethyl*-p-*toluidine* is an oil boiling at 169° under 20 mm. pressure; its *hydrobromide* crystallises in needles melting at 185°. The *perbromide*,

$$C_6H_2MeBr_2\cdot NHEt,HBr,Br_2,$$

crystallises in golden-yellow needles melting at 110°, and is converted into 3 : 5-dibromo-*p*-toluidine by warming with water.

p-Bromodimethylaniline is formed easily from dimethylaniline and bromine in acetic acid solution; its *hydrobromide* crystallises in prisms melting at 105° and decomposing at 185°, and the *hydriodide* forms crystals melting at 145°. 2 : 4-*Dibromodimethylaniline*,

$$C_6H_3Br_2\cdot NMe_2,$$

is prepared by treating dimethylaniline with excess of bromine in acetic acid solution and then decomposing the perbromide thus formed with sodium acetate, or directly by methylating dibromoaniline or dibromomethylaniline; it is an oil boiling at 275° under 740 mm. pressure; its *stannochloride* crystallises in plates decomposing at 240°, and its *platinichloride* in golden-yellow needles melting at 237°; the *hydrobromide* crystallises in prisms. 2 : 4 : 6-*Tribromodimethylaniline*, prepared by methylating tribromomethylaniline with methyl sulphate and magnesium oxide, is an oil boiling at 301° under 750 mm. pressure; it reacts with bromine, giving tribromomethylaniline, but not with methyl iodide or methyl sulphate; the *platinichloride* crystallises in prisms sintering at 180° and melting at 190°. The *perbromide* from dimethylaniline, $NPhMe_2,HBr,Br_2$, forms reddish-brown crystals which are easily reduced to dimethylaniline and are readily converted into *p*-bromodimethylaniline. The *perbromide*,

$(C_6H_4Br{\cdot}NMe_2,HBr)_2Br_2$, is prepared directly from dimethylaniline in acetic acid solution, and forms dark red crystals, sintering at 95° and melting at 107°. The *perbromide*, $C_6H_4Br{\cdot}NMe_2,HBr,Br_2$, is formed when 1 mol. of dimethylaniline and 2 mols. of bromine are used; it crystallises in dark red plates sintering at 75° and melting at 85°; on keeping in the air it passes over into the perbromide last mentioned. With water it yields the dibromodimethylaniline and the *perbromide* of diphenoquinonetetramethyldi-iminium dibromide; the latter is also formed from bromine and tetramethylbenzidine; it is a brownish-red powder melting at about 158°, is reduced to tetramethylbenzidine, and is coloured bluish-green by alkali hydroxides. Tetramethylbenzidine also gives with bromine a dark green, amorphous *compound*, $C_{16}H_{20}N_2Br_2$, which sinters at 70° and melts at 90°, and is reduced to tetramethylbenzidine; concentrated sulphuric or hydrochloric acids give red, crystalline products, and bromine converts it into the perbromide last mentioned. Dibromodimethylaniline hydrobromide is converted by bromine into the *perbromide*,

$$(C_6H_3Br_2{\cdot}NMe_2,HBr)_4Br_2,$$

which crystallises in green plates melting at 135°. The same salt also yields the *perbromide*, $C_6H_3Br_2{\cdot}NMe_2,HBr,Br_2$, which crystallises in prisms melting at 102°. The *perbromide*, $C_6H_2Br_3{\cdot}NMe_2,HBr,Br_2$, prepared from tribromodimethylaniline, crystallises in pale yellowish-red needles melting at 124°, and is converted by water into tribromomethylaniline.

5-*Bromodimethyl*-o-*toluidine*, $C_6H_3MeBr{\cdot}NMe_2$, boils at 246°, its *platinichloride* crystallises in golden-yellow prisms decomposing at 240°. 3 : 5-*Dibromodimethyl*-o-*toluidine*, prepared by alkylating dibromotoluidine, is an oil boiling at 277° under 751 mm. pressure; it does not react either with methyl iodide or methyl sulphate, and when treated with bromine in acetic acid solution yields *dibromomethyltoluidine*, a methyl group being eliminated; the last-mentioned base is also directly produced by the action of bromine on dimethyl-*o*-toluidine, and decomposing the perbromide first formed with sodium acetate; it is an oil boiling at 185—187° under 50 mm. pressure, and forms a *hydrobromide* which crystallises in plates decomposing at 220°. Dimethyl-*o*-toluidine forms the *perbromide*, $C_6H_4Me{\cdot}NMe_2,HBr,Br_2$, which crystallises in needles or plates melting at 68°, and is converted by treatment with solvents into 5-bromodimethyl-*o*-toluidine. The *perbromide*, $(C_6H_3MeBr{\cdot}NMe_2,HBr)_2Br_2$, prepared from 1 mol. of dimethyl-*o*-toluidine and 1½ mols. of bromine, crystallises in dark red needles and is converted by water into a mixture of bromodimethyl- and dibromomethyl-*o*-toluidine. The *perbromide*,

$$C_6H_2MeBr_2{\cdot}NMe_2,HBr,Br_2,$$

obtained from dimethyl-*o*-toluidine and 2 mols. of bromine, crystallises in plates or prisms melting at 85° and decomposing at 140°. The *perbromide*, $C_6H_2MeBr_2{\cdot}NMe_2,HBr,Br_2$, crystallises in yellowish-red needles melting at 112°, and is converted by water into dibromomethyltoluidine.

3-*Bromodimethyl*-p-*toluidine*, prepared by brominating dimethyl-*p*-toluidine, is an oil boiling at 239° under 750 mm. pressure, and is converted by bromine into the 3 : 5-*dibromomonomethyl*-p-*toluidine*, which boils at 154° under 16 mm. pressure. 3 : 5-*Dibromodimethyl*-p-*toluidine*, prepared by methylating the dibromotoluidine, is an oil boiling at 270° under 750 mm. pressure. The *perbromide*,

$$C_6H_2MeBr_2\cdot NMe_2,HBr,Br_2,$$

crystallises in prisms melting at 130°, and on treatment with water loses methyl bromide.

2 : 4-*Dibromodiethylaniline*, $C_6H_3Br_2\cdot NEt_2$, formed on treating with sodium acetate the perbromide produced by the action of bromine on diethylaniline, is an oil boiling at 285° under 751 mm. pressure; it is converted by further treatment with bromine into *s*-tribromoaniline; its *platinichloride* crystallises in yellowish-red prisms melting at 207°, and its *stannochloride* forms crystals melting at 235°. The *perbromide*, $NPhEt_2,HBr,Br_2$, is a red oil, which is converted by water into *p*-bromodiethylaniline. The *perbromide*, $(C_6H_4Br\cdot NEt_2,HBr)_2Br_2$, crystallises in prisms melting at 75°, and is converted by water into 2 : 4-dibromodiethylaniline and a quinonoid derivative of tetraethylbenzidine. Diethylaniline also yields the *perbromide*, $(C_6H_4Br\cdot NEt_2,HBr)_4Br_6$, which crystallises in red prisms melting at 81°.

4 : 4′-*Dibromodiphenylmethylamine*, $C_{13}H_{11}NBr_2$, prepared from diphenylmethylamine and bromine, crystallises in needles melting at 120°. 2 : 2′ : 4 : 4′-*Tetrabromodiphenylmethylamine*, $C_{13}H_9NBr_4$, prepared by warming the perbromide formed from diphenylmethylamine with the solvent, crystallises in prisms melting at 142°; bromine converts it into tetrabromodiphenylamine. Dibromodiphenylmethylamine yields a *perbromide*, $(C_6H_4Br)_2NMe,HBr,Br_2$ (?), which forms red crystals, and is transformed by solvents into a mixture of tetrabromodiphenylmethylamine and tetrabromodiphenylamine.

The *perbromide*, $NPhMe_3Br,Br_4$, prepared from phenyltrimethylammonium bromide, crystallises in bluish-red prisms melting at 40°, and is converted into the dibromide on exposure to the air. p-*Tolyltrimethylammonium bromide* crystallises in prisms melting at 219°, and is converted by bromine into the *perbromide*, $C_6H_4Me\cdot NMe_3Br,Br_2$, which forms yellow, four-sided plates melting at 113°, from which, by further treatment with bromine, the *perbromide*,

$$C_6H_4Me\cdot NMe_3Br,Br_4,$$

is obtained; it forms dark red crystals melting at 45°. K. J. P. O.

Crystalline Forms of the 2 : 4-Dinitroaniline Derivatives Substituted in the NH_2-Group. Frans M. Jaeger (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, **9**, 23—25).—The melting points, molecular weights, equivalent volumes in the solid state, symmetry, axial elements, and topic parameters of 31 derivatives of 2 : 4-dinitroaniline are recorded in tabular form. The substances all have the same family character, only a few showing no simple relationship to the rest. E. F. A.

Nitration of Acetanilide. Arnold F. Holleman and C. H. Sluiter (*Rec. trav. chim.*, 1906, **25**, 208—212).—The authors have examined the products of the nitration of acetanilide in order to determine if the quantity of the secondary products is affected by the concentration of the nitric acid employed (compare Körner, this Journal, 1876, i, 204);

the results show that when acetanilide is slowly added to ten times its weight of nitric acid of sp. gr. 1·46 at 0°, the product is pure *p*-nitroacetanilide; if nitric acid of a higher specific gravity is employed, 2 : 4-dinitroacetanilide is formed as a secondary product, the quantity increasing with the increase in the concentration of the nitric acid, but no *o*-nitroacetanilide is produced (compare Körner, *loc. cit.*; Beilstein and Kurbatoff, *Annalen*, 1879, **197**, 83); if, however, acetanilide is added rapidly to nitric acid of sp. gr. 1·52, a small quantity of *o*-nitroacetanilide is formed owing to the increase in temperature caused by the more violent reaction. M. A. W.

Thio-fatty Anilides. HEINRICH BECKURTS and GUSTAV FRERICHS (*J. pr. Chem.*, 1906, [ii], **74**, 25—50. Compare Abstr., 1902, i, 763). —[With L. HARTWIG.]—*Methylthiolacetanilide*, $SMe\cdot CH_2\cdot CO\cdot NHPh$, prepared by the action of methyl iodide and alcoholic potassium hydroxide on thioglycollanilide in a sealed tube in the water-bath, crystallises in colourless leaflets, melts at 74°, and is readily soluble in alcohol or ether. n-*Propylthiolacetanilide*, $SPr^{\alpha}\cdot CH_2\cdot CO\cdot NHPh$, crystallises in colourless needles and melts at 57°. iso*Propylthiolacetanilide*, $SPr^{\beta}\cdot CH_2\cdot CO\cdot NHPh$, forms flat needles and melts at 67°. *Ethylenedithioldiacetanilide*, $C_2H_4(S\cdot CH_2\cdot CO\cdot NHPh)_2$, crystallises in colourless needles, melts at 158°, and is only sparingly soluble in cold alcohol. *Propylenedithioldiacetanilide*, $C_3H_6(S\cdot CH_2\cdot CO\cdot NHPh)_2$, forms colourless needles and melts at 154—155°. *Carboxymethylthiolacetanilide*, $CO_2Me\cdot S\cdot CH_2\cdot CO\cdot NHPh$, formed from methyl chlorocarbonate and thioglycollanilide, crystallises in colourless needles, melts at 83°, and is readily soluble in alcohol. *Benzylthiolacetanilide*,

$$CH_2Ph\cdot S\cdot CH_2\cdot CO\cdot NHPh,$$

forms colourless, flat needles, melts at 73·5°, and is readily soluble in alcohol. *Benzylidenedithioldiacetanilide*, $CHPh(S\cdot CH_2\cdot CO\cdot NHPh)_2$, formed by the action of benzaldehyde or of benzylidene dichloride and potassium hydroxide on thioglycollanilide, crystallises in colourless needles and melts at 182°. *Nitrosothiolacetanilide*,

$$NO\cdot S\cdot CH_2\cdot CO\cdot NHPh,$$

formed by the action of potassium nitrite and hydrochloric acid on thioglycollanilide in aqueous solution, crystallises in red needles, decomposes when heated, yielding nitric oxide and dithioglycollanilide, and is readily soluble in alcohol or ether.

Thioglycollanilide forms a *mercuric* derivative,

$$Hg(S\cdot CH_2\cdot CO\cdot NHPh)_2,$$

which crystallises in glistening leaflets and decomposes when heated, and a *mercurichloride*, $HgCl\cdot S\cdot CH_2\cdot CO\cdot NHPh$, which is obtained as a yellowish-white, crystalline powder, insoluble in the ordinary solvents.

α-Methylthiolpropanilide, $SMe\cdot CHMe\cdot CO\cdot NHPh$, formed by the action of methyl iodide and potassium hydroxide on α-thiolpropanilide in alcoholic solution, crystallises in glistening, colourless needles and melts at 126°. *α-*n*-Propylthiolpropanilide*, $SPr^{\alpha}\cdot CHMe\cdot CO\cdot NHPh$, crystallises in needles and melts at 92°. *α-*iso*Propylthiolpropanilide*, $C_{12}H_{17}ONS$, forms colourless needles melting at 84°. *Ethylenedi-α-thioldipropanilide*, $C_2H_4(S\cdot CHMe\cdot CO\cdot NHPh)_2$, crystallises in colourless needles melting at 172—174°. *Propylenedi-α-thioldipropanilide*,

$C_3H_6(S\cdot CHMe\cdot CO\cdot NHPh)_2$, forms a slightly yellow, viscid oil. *a-Carboxymethylthiolpropanilide*, $CO_2Me\cdot S\cdot CHMe\cdot CO\cdot NHPh$, crystallises in glistening leaflets and melts at 103·5°. *a-Benzylthiolpropanilide*, $CH_2Ph\cdot S\cdot CHMe\cdot CO\cdot NHPh$, crystallises in colourless, flat needles and melts at 119·5°. *Benzylidenedi-a-thioldipropanilide*, $CHPh(S\cdot CHMe\cdot CO\cdot NHPh)_2$, forms colourless needles and melts at 187°. *a-Nitrosothiolpropanilide*, $NO\cdot S\cdot CHMe\cdot CO\cdot NHPh$, is obtained as an unstable red oil. The *mercuric* derivative,

$$Hg(S\cdot CHMe\cdot CO\cdot NHPh)_2,$$

separates from glacial acetic acid in small crystals and melts and decomposes above 200°. The *mercurichloride*, $HgCl\cdot S\cdot CHMe\cdot CO\cdot NHPh$, forms a crystalline powder and melts and decomposes at 110—120°.

a-Methylthiolbutyranilide, $SMe\cdot CHEt\cdot CO\cdot NHPh$, crystallises in colourless needles and melts at 111—112°. *a-*iso*Propylthiolbutyranilide*, $SPr^{\beta}\cdot CHEt\cdot CO\cdot NHPh$, forms colourless, flat needles and melts at 87—88°. *Ethylenedi-a-thioldibutyranilide*,

$$C_2H_4(S\cdot CHEt\cdot CO\cdot NHPh)_2,$$

forms colourless crystals melting at 125°. *Propylenedi-a-thioldibutyranilide*, $C_3H_6(S\cdot CHEt\cdot CO\cdot NHPh)_2$, is obtained as a viscid, yellow oil which gradually crystallises. *a-Carboxymethylthiolbutyranilide*, $CO_2Me\cdot S\cdot CHEt\cdot CO\cdot NHPh$, forms colourless needles melting at 82°. *a-Benzylthiolbutyranilide*, $CH_2Ph\cdot S\cdot CHEt\cdot CO\cdot NHPh$, crystallises in colourless needles melting at 89°. *Benzylidenedi-a-thioldibutyranilide*, $CHPh(S\cdot CHEt\cdot CO\cdot NHPh)_2$, forms colourless leaflets melting at 148°. *a-Nitrosothiolbutyranilide*, $NO\cdot S\cdot CHEt\cdot CO\cdot NHPh$, is obtained as an unstable red oil. The *mercuric* derivative, $Hg(S\cdot CHEt\cdot CO\cdot NHPh)_2$, and the *mercurichloride*, $HgCl\cdot S\cdot CHEt\cdot CO\cdot NHPh$, form micro-crystalline powders which decompose when heated.

[With CARL BEYER.]—*Carbamylthiolaceto-*o*-toluidide*,

$$NH_2\cdot CO\cdot S\cdot CH_2\cdot CO\cdot NH\cdot C_7H_7,$$

prepared by heating chloroacetic acid and *o*-toluidine with potassium thiocyanate in aqueous solution, crystallises in colourless needles, melts at 123—124°, and when dissolved in hot 10 per cent. ammonia and precipitated by hydrochloric acid in an atmosphere of carbon dioxide yields *thiolaceto-*o*-toluidide*, $SH\cdot CH_2\cdot CO\cdot NH\cdot C_7H_7$, which crystallises in colourless needles, melts at 84—85°, and is readily soluble in alcohol. *Dithiodiaceto* o*-toluidide*, $S_2(CH_2\cdot CO\cdot NH\cdot C_7H_7)_2$, crystallises in colourless needles melting at 164—165°. The following derivatives of thiolaceto-*o*-toluidide, in which $R = \cdot S\cdot CH_2\cdot CO\cdot NH\cdot C_7H_7$, have been prepared; the temperatures given are melting points: *methyl-*, $Me\cdot R$: colourless leaflets, 65—66°; *ethyl-*, $Et\cdot R$: colourless needles, 60—61°; *ethylenedi-*, $C_2H_4R_2$: colourless nodules, 184—185°; *dimethylmethylenedi-*, CMe_2R_2: colourless leaflets, 160—161°; n-*propyl*, $Pr^{a}\cdot R$, colourless needles, 57—58°; iso*propyl-*, $CHMe_2R$: colourless needles, 61—62°; *benzyl-*, $CH_2Ph\cdot R$: colourless needles, 74—75°; *carboxymethyl-*, $CO_2Me\cdot R$: colourless needles, 90—91°; *carboxyethyl-*, $CO_2Et\cdot R$: colourless needles, 78—79°.

*Thioldiaceto-*o*-toluidamic acid*, $CO_2H\cdot CH_2\cdot S\cdot CH_2\cdot CO\cdot NH\cdot C_7H_7$, formed from chloroacetic acid and thiolaceto-*o*-toluidide, crystallises in colourless nodules, melts at 125—126°, and is readily soluble in alcohol. The *methyl*, $CO_2Me\cdot CH_2\cdot S\cdot CH_2\cdot CO\cdot NH\cdot C_7H_7$, and *ethyl*,

$$CO_2Et\cdot CH_2\cdot S\cdot CH_2\cdot CO\cdot NH\cdot C_7H_7,$$

esters form viscid, yellow oils. The *amide*,

$$NH_2\cdot CO\cdot CH_2\cdot S\cdot CH_2\cdot CO\cdot NH\cdot C_7H_7,$$

forms colourless needles and melts at 150—151°. Thioldiacetodi-*o*-toluidide, formed from thiolaceto-*o*-toluidide and chloroacetyl-*o*-toluidide, is identical with Grothe's product from chloroacetyl-*o*-toluidide and potassium hydrogen sulphide (Abstr., 1901, i, 79).

Thiolaceto-m-*toluidide*, $SH\cdot CH_2\cdot CO\cdot NH\cdot C_7H_7$, crystallises in colourless needles and melts at 152—153°. *Dithiodiaceto*-m-*toluidide*,

$$S_2(CH_2\cdot CO\cdot NH\cdot C_7H_7)_2,$$

forms colourless needles and melts at 162—163°. The following derivatives of thiolaceto-*m*-toluidide, in which $R = \cdot S\cdot CH_2\cdot CO\cdot NH\cdot C_7H_7$, are described; the temperatures given are melting points:

Carbamyl-, $NH_2\cdot CO\cdot R$: colourless needles, 151—152°; *methyl-*, $Me\cdot R$: colourless needles, 52—53°; *ethyl-*, $Et\cdot R$: a yellow oil; *ethylenedi-*, $C_2H_4R_2$: colourless needles, 127—128°; *hydroxyethyl-*, $OH\cdot CH_2\cdot CH_2\cdot R$: colourless needles, 89—90°; *dimethylmethylenedi-*, CMe_2R_2: colourless leaflets, 141—142°; *benzyl-*, $CH_2Ph\cdot R$: colourless needles, 39—40°, *carboxymethyl-*, $CO_2Me\cdot R$: a viscid oil; *carboxyethyl-*, $CO_2Et\cdot R$: colourless leaflets, 82—83°.

Thiodiaceto-m-*toluidamic acid*, $CO_2H\cdot CH_2\cdot S\cdot CH_2\cdot CO\cdot NH\cdot C_7H_7$, forms colourless leaflets melting at 99—100°. The *methyl*, $C_{12}H_{15}O_3NS$, and *ethyl*, $C_{13}H_{17}O_3NS$, esters are obtained as viscid, yellow oils. The *amide*, $NH_2\cdot CO\cdot CH_2\cdot S\cdot CH_2\cdot CO\cdot NH\cdot C_7H_7$, crystallises in colourless nodules and melts at 97—98°. *Thiodiaceto*-m-*toluidide*,

$$S(CH_2\cdot CO\cdot NH\cdot C_7H_7)_2,$$

crystallises in colourless needles and melts at 135—136°.

Thiolaceto-p-*toluidide*, $C_9H_{11}ONS$, crystallises in colourless needles and melts at 125—126°. *Dithiodiaceto*-p-*toluidide*,

$$S_2(CH_2\cdot CO\cdot NH\cdot C_7H_7)_2,$$

crystallises in colourless needles and melts at 180—182°. The following derivatives of thiolaceto-*p*-toluidide, $R = \cdot S\cdot CH_2\cdot CO\cdot NH\cdot C_7H_7$, are described; the temperatures given are melting points:

Carbamyl-, $NH_2\cdot CO\cdot R$: colourless leaflets, 196°; *methyl-*, $Me\cdot R$: colourless needles, 102—103°; *ethyl-*, $Et\cdot R$: colourless needles, 84—85°; ethylenedi-, $C_2H_4R_2$: colourless needles, 194—195°; *hydroxyethyl-*, $OH\cdot CH_2\cdot CH_2\cdot R$: colourless needles, 87—88°; *dimethylmethylenedi-*, CMe_2R_2: colourless needles, 182—183°; n-*propyl-*, $Pr^{\alpha}\cdot R$: colourless needles, 80—81°; iso*propyl-*, $Pr^{\beta}\cdot R$: colourless needles, 66—67°; *benzyl-*, $CH_2Ph\cdot R$: colourless needles, 73—74°; *benzylidenedi-*, $CHPhR_2$: colourless needles, 185—186°; *carboxymethyl-*, $CO_2Me\cdot R$: 96—97°; *carboxyethyl-*, $CO_2Et\cdot R$: colourless needles, 126—127°.

Thiodiaceto-p-*toluidamic acid*, $C_{11}H_{13}O_3NS$, forms colourless crystals and melts at 101—102°. The *methyl* ester, $C_{12}H_{15}O_3NS$, melts at 38—39°; the *ethyl* ester, $C_{13}H_{17}O_3NS$, melts at 46—47°; the *amide*, $NH_2\cdot CO\cdot CH_2\cdot S\cdot CH_2\cdot CO\cdot NH\cdot C_7H_7$, crystallises in colourless leaflets and melts at 148—149°. G. Y.

Direct Introduction of Amino-groups into the Nucleus of Aromatic Nitro-compounds. JAKOB MEISENHEIMER and EGBERT PATZIG (*Ber.*, 1906, **39**, 2533—2542).—The action of hydroxylamine hydrochloride on *m*-dinitrobenzene in alcoholic sodium ethoxide solution leads to the formation of a light red *sodium* salt, $C_6H_8O_6N_4Na_2$, which detonates slightly when heated or on contact with a small quantity of water, is more stable in the presence of an alkali hydroxide, and on acidification yields *m*-dinitrobenzene. The cooled aqueous solution of the sodium salt gradually deposits *m*-dinitro-*m*-phenylenediamine, whilst the diluted aqueous-alcoholic solution yields *m*-dinitro-*m*-phenylenediamine, *m*-dinitrobenzene, and 2 : 4-dinitroaniline, which is converted into *m*-dinitro-*m*-phenylenediamine by the further action of hydroxylamine.

The *sodium* salt, $C_7H_{11}O_9N_6Na_3,3H_2O$, obtained in the same manner from *s*-trinitrobenzene as an intensely red, granular precipitate, gradually decomposes in a vacuum, forming ammonia, detonates when heated, and yields picramide and *s*-trinitro-*m*-phenylenediamine on addition of an acid to its aqueous solution at 0°.

2 : 6-*Dinitro-3-toluidine*, $C_7H_7O_4N_3$, is obtained in a 10—15 per cent. yield by the action of hydroxylamine hydrochloride on 2 : 6-dinitrotoluene in methyl-alcoholic potassium hydroxide solution at 30° and addition of much water to the resulting solution; it forms glistening, yellow crystals, melts at 132·5°, and is readily soluble in alcohol.

2-Nitro-α-naphthylamine is formed in the same manner from β-nitronaphthalene; if the product is allowed to remain in contact with the reaction solution, it is converted slowly into 2-nitro-α-naphthol.

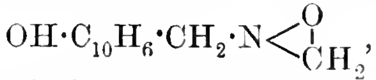
The action of hydroxylamine on ethyl *m*-nitrobenzoate in concentrated, alkaline, absolute alcoholic solution leads to the formation of the *sodium* salt of *m*-nitrobenzhydroxamic acid, $C_7H_5O_4N_2Na$; the acid melts at 153° (m. p. 151°: Werner and Skiba, Abstr., 1899, i, 690). *m*-Nitrobenzaldehyde and hydroxylamine react in alkaline solution, forming *m*-nitrobenzaldoxime melting at 123° (121°: Ciamician and Silber, Abstr., 1904, i, 161; 119°: Gabriel, Abstr., 1883, 581, 919). G. Y.

Action of Benzylamine on Ethyl α-Crotonate. Giovanni Sani (*Atti R. Accad. Lincei*, 1906, [v], **15**, i, 645—646).—The *benzylamide* of *benzylaminobutyric acid*,

$$CH_2Ph{\cdot}NH{\cdot}CHMe{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH_2Ph,$$

prepared by heating ethyl α-crotonate (1 mol.) and benzylamine (2 mols.) with absolute alcohol in a sealed tube at 150°, separates from ether in shining, well-developed, rhombic crystals [Artini: $a:b:c = 1{\cdot}1113:1:0{\cdot}4774$], melts at 115—116°, and is soluble in alcohol. T. H. P.

Reaction between β-Naphthol, Formaldehyde, and Hydroxylamine. Mario Betti (*Gazzetta*, 1906, **36**, i, 388—401. Compare Abstr., 1904, i, 581).—The action of formaldehyde and hydroxylamine on an alcoholic solution of β-naphthol yields a *compound*,

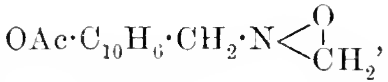


$$OH{\cdot}C_{10}H_6{\cdot}CH_2{\cdot}N{<}\begin{matrix}O\\|\\CH_2\end{matrix},$$

which crystallises from alcohol in mammillary masses of slender, white needles, melting and decomposing at 149°, and dissolves in benzene, chloroform, or dilute sodium hydroxide solution, and sparingly in light petroleum; the cold alcoholic solution gives an intense reddish-brown coloration with aqueous ferric chloride. If the reaction proceeds in neutral or alkaline solution, the above compound is accompanied by methylenedinaphthol.

In alcoholic solution, the compound melting at 149° is transformed, slowly in the cold and more rapidly on boiling, into *di-β-naphthol-methylenehydroxylamine*, $OH\cdot N(CH_2\cdot C_{10}H_6\cdot OH)_2$, which crystallises from alcohol in shining, straw-yellow rhombohedra melting and decomposing at 227°, and dissolves sparingly in all organic solvents. On boiling with 20 per cent. hydrochloric acid, the compound melting at 149° is converted into *di-β-naphtholmethylenehydroxylamine hydrochloride*, $C_{22}H_{19}O_3N,HCl$, which forms a crystalline powder with an ill-defined melting point above 200°.

By treating with sodium hydroxide solution and subsequently saturating the liquid with carbon dioxide, the compound is converted into methylenedi-β-naphthol and di-β-naphtholmethylenehydroxylamine.



The *acetyl* derivative, $OAc\cdot C_{10}H_6\cdot CH_2\cdot N\langle{}^{O}_{CH_2}$, crystallises from alcohol in shining prisms melting at 130°, and exhibits normal cryoscopic behaviour in acetic acid solution.

Dibenzoyl-β-naphtholmethylenehydroxylamine,

$$OBz\cdot C_{10}H_6\cdot CH_2\cdot NBz\cdot OH,$$

prepared by the action of benzoyl chloride on the compound melting at 149°, dissolved in sodium hydroxide solution, separates from a mixture of alcohol and benzene in highly refractive, shining rhombohedra melting at 177°.

β-Naphtholmethyleneamine, $OH\cdot C_{10}H_6\cdot CH_2\cdot NH_2$, obtained by reducing the crude compound melting at 149° by means of zinc dust and hydrochloric acid, crystallises from light petroleum in colourless needles melting at 115—116° and reddens and oxidises slowly in the air, and more rapidly in a faintly alkaline solution. The *hydrochloride*, $C_{11}H_{11}ON,HCl$, crystallises from a mixture of alcohol and hydrochloric acid in white needles melting and decomposing at 226—227°.

Di-β-naphtholmethyleneamine, $NH(CH_2\cdot C_{10}H_6\cdot OH)_2$, also obtained by reducing the crude compound melting at 149°, crystallises from aqueous alcohol in white, prismatic needles melting at 163°. The *hydrochloride*, $C_{22}H_{19}O_2N,HCl$, separates from alcohol, acidified with hydrochloric acid, in colourless, rhombohedral crystals melting and decomposing at 220°.

T. H. P.

Isomerism of *ar*-Thio-compounds. OSCAR HINSBERG (*Ber.*, 1906, **39**, 2427—2436. Compare Abstr., 1905, i, 518).—The dithioaniline melting at 76—77° is now found to be identical with Schmidt's 4 : 4′-dithioaniline melting at 78—79° (m. p. 80°; Hofmann, Abstr., 1895, i, 132). It forms two acetyl derivatives: that melting at 182° is labile, and changes slowly at the ordinary temperature into the stable acetate melting at 215—216°. *Dibenzylidenedithioaniline*,

$$CHPh:N\cdot C_6H_4\cdot S_2\cdot C_6H_4\cdot N:CHPh,$$

is obtained in only one modification, which crystallises from alcohol in yellow needles, melts at 136°, and yields benzaldehyde when treated with dilute mineral acids.

The reduction of 4 : 4′-dithioaniline with zinc dust and hydrochloric acid leads to the formation of a solution containing *p*-aminophenyl mercaptan, which is oxidised on exposure to air, forming 4 : 4′-dithioaniline, and, on addition of acetic acid, separates as an oil; this has an unpleasant odour and is soluble in mineral acids or aqueous alkali hydroxides.

p-Acetylaminophenyl mercaptan, $SH\cdot C_6H_4\cdot NHAc$ (Hofmann, Abstr., 1894, i, 87), is obtained on boiling 4 : 4′-dithioacetanilide with aluminium powder and acetic acid as a mixture of two modifications, crystallising in small, yellow leaflets. The colourless form obtained on adding hydrochloric acid to a cold alkaline solution of the mixture crystallises in white scales, commences to sinter at about 145°, melts at 154°, has in aqueous solution a slight mercaptan odour, and reddens litmus. With lead acetate, it gives a chocolate-brown, with silver nitrate a yellow precipitate, and is oxidised by air to 4 : 4′-dithioacetanilide melting at 215—216°, or by ferric chloride and a small quantity of hydrochloric acid to a mixture of the two isomerides melting at 160—215°. The yellow modification of *p*-acetylaminophenyl mercaptan is obtained on cooling the hot saturated aqueous solution of the mixture to 70°; it forms yellowish-red leaflets or flat prisms and melts at 154°. Dilute solutions or concentrated solutions below 70° deposit the colourless modification. The conversion of the colourless into the yellow form takes place also slowly at 100—137° on exposure to sunlight, or quickly on crystallisation from methyl or ethyl alcohol.

p-*Acetylaminophenyl methyl thioether*, $SMe\cdot C_6H_4\cdot NHAc$, is formed by treating the lead or silver salt with methyl iodide at the ordinary temperature, by heating the mercaptan with methyl iodide and sodium hydroxide in alcohol solution, by heating the sodium mercaptide with potassium methyl sulphate and methyl alcohol at 170°, or by the action of methyl iodide on the mercaptan in pyridine solution. It crystallises in colourless leaflets or thin needles, melts at 128°, and is readily soluble in alcohol, ether, or glacial acetic acid.

Diacetyl-p-*aminophenyl mercaptan*, $SAc\cdot C_6H_4\cdot NHAc$, formed by the action of acetic anhydride on the aminomercaptan in aqueous sodium hydroxide solution, crystallises in colourless leaflets and melts at 144°.

Dithiobenzanilide, $NHBz\cdot C_6H_4\cdot S_2\cdot C_6H_4\cdot NHBz$, formed by heating dithioaniline with benzoic anhydride, is obtained as a colourless, crystalline powder melting at 264°. When heated with aluminium powder, glacial acetic acid, and a small amount of concentrated hydrochloric acid, it yields a mixture of two *p*-benzoylaminophenyl mercaptans. The *colourless* modification, $NHBz\cdot C_6H_4\cdot SH$, is obtained by adding hydrochloric acid to the cold alkaline solution of the mixture; it crystallises in small leaflets, commences to sinter at 165°, melts at 180°, gives precipitates with lead acetate and silver nitrate, and on oxidation with ferric chloride or potassium ferrocyanide and sodium hydroxide yields dithiobenzanilide. The *yellow* modification, obtained by heating the colourless form or by crystallising it from alcohol, forms large, yellow needles and melts at 182°. Both modifications form colourless solutions.

The structure of these isomeric modifications of the acylaminophenyl mercaptans is discussed. G. Y.

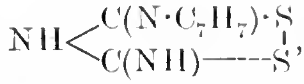
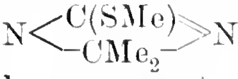
Conversion of α-Nitro-β-phenyl-α-methylcarbamide into s-Nitrophenylmethylcarbamide. ROLAND SCHOLL and B. NYBERG (*Ber.*, 1906, **39**, 2491—2494. Compare Scholl and Holdermann, *Annalen*, 1906, **345**, 382).—The additive compound obtained from methylnitroamine and phenylcarbimide has the formula $NHPh\cdot CO\cdot NMe\cdot NO_2$, for by treatment at 0° with concentrated sulphuric acid a mixture of *s*-*o*-nitrophenylmethylcarbamide and *p*-nitrophenylmethylcarbamide is obtained, and is separated by hot 1 per cent. sodium hydroxide solution, in which the former compound is more easily soluble. The orientation of the NO_2 group is determined by heating the compounds with hydrochloric acid at 120—130°, whereby *o*- and *p*-nitroaniline respectively are obtained.

α-Nitro-β-phenyl-α-methylcarbamide yields with phenol at 100° *phenyl phenylcarbamate*, which forms colourless needles and melts at 125·5°; with aniline, it forms *s*-diphenylcarbamide. C. S.

Unsaturated Disulphides. EMIL FROMM (*Annalen*, 1906, **348**, 144—160. Compare Abstr., 1895, i, 605; Hantzsch and Wolvekamp, Abstr., 1904, i, 718).—Disulphides which are decomposed with separation of sulphur on heating or on treatment with water, alkalis, ammonia, or amines, contain the grouping $-\ddot{C}\cdot S\cdot S\cdot\ddot{C}-$, and are not necessarily cyclic disulphides. The double linkings may connect the carbon atoms with similar atoms or groups, as in ethyl dioxythiocarbonate, $S{:}C(OEt)\cdot S\cdot S\cdot C(OEt){:}S$, dibenzoyl sulphide, $O{:}CPh\cdot S\cdot S\cdot CPh{:}O$, or phenylthiouret,  $NH\!\left<\begin{matrix}C({:}NPh)-\\C({:}NH)-\end{matrix}\right>\!S_2$, or with dissimilar atoms or groups, as in perthiocyanic acid,  $NH\!\left<\begin{matrix}C({:}NH)-\\C({:}S)-\end{matrix}\right>\!S_2$. The reaction is often complicated by the interaction of the primary products. If the double linkings are part of stable ring systems, as in diphenyl disulphide, $SPh\cdot SPh$, or the thiodiazolone disulphides (Busch, Abstr., 1896, i, 190), the decomposition by means of alkalis takes place, but without separation of sulphur. Disulphides which do not contain the above grouping are stable towards alkalis.

The author discusses the constitution of the sulphides and oxides of the thiocarbimides which, as represented by Freund (Abstr., 1895, i, 576), form exceptions to this rule. G. Y.

Dithiobiurets. EMIL FROMM and KURT SCHNEIDER (*Annalen*, 1906, **348**, 161—174. Compare Fromm, Abstr., 1893, i, 575).—Perthiocyanic acid reacts with *p*-toluidine, *o*-toluidine, *as*-*m*-xylidine, and *o*-phenetidine, forming the thiobiurets, thiocarbamides, and sulphur. The dithiobiurets, which are isolated by extraction with cold dilute alkali hydroxides, are oxidised by iodine, forming the thiourets, which are bases, and when heated with concentrated hydrochloric acid at 165° yield 2-aminobenzothiazoles.

p-Tolyldithiobiuret melts at 173·5° (159°; Tursini, Abstr., 1884, 1140) and forms p-*tolylthiouret hydriodide*,  $NH<\begin{matrix}C(N\cdot C_7H_7)\cdot S\\ C(NH)\text{------}S\end{matrix},HI$, separating in yellow crystals and melting at 221·5°. Contrary to Tursini's statement (*loc. cit.*), *p*-tolyldithiobiuret reacts with 1 mol. of methyl iodide to form *methyl*-p-*tolyl-ψ dithiobiuret*, $C_{10}H_{13}N_3S_2$, which crystallises in nodular aggregates of needles and melts at 125·5°. With 2 mols. of methyl iodide, it forms *dimethyl*-p-*tolyl-ψ-dithiobiuret*, $C_7H_7\cdot N\colon C(SMe)\cdot NH\cdot C(SMe)\colon NH$, which crystallises in white needles, melts at 67°, and evolves mercaptan at 100°. When treated with acetone and hydrogen chloride, this forms *methyl*-p-*tolyldimethyl-ψ-dithioketuret*, $C_6H_4Me\cdot N\colon C(SMe)\cdot$$N<\begin{matrix}C(SMe)\\ -CMe_2-\end{matrix}>N$, which crystallises in white needles and melts and decomposes at 164°. p-*Tolyl-ψ-thiobenzylcyanocarbamide*, $C_7H_7\cdot NH\cdot C(SC_7H_7)\colon N\cdot CN$, prepared by heating *p*-tolyldithiobiuret with sodium hydroxide and benzyl chloride in alcoholic solution, crystallises in glistening, white scales and melts at 181·5°.

o-*Tolyldithiobiuret*, $C_9H_{11}N_3S_2$, crystallises in stout needles and melts at 159°. o-*Tolylthiouret hydriodide*, $C_9H_9N_3S_2,HI,C_2H_6O$, crystallises from alcohol in yellow needles and melts at 153°. o-*Tolyl-ψ-thiobenzylcyanocarbamide*, $C_{16}H_{16}N_3S$, forms a white, crystalline powder and melts at 165°.

m-*Xylyldithiobiuret*, $C_{10}H_{13}N_3S_2$, forms yellow crystals and melts at about 129°. m-*Xylylthiouret hydriodide*, $C_{10}H_{11}N_3S_2,HI$, crystallises in yellow needles and melts at 146°.

o-*Methoxyphenyldithiobiuret*, $C_{10}H_{13}ON_3S_2$, forms long, yellow needles and melts at 153°. o-*Methoxyphenylthiouret hydriodide*,

$$C_{10}H_{11}ON_3S_2,HI,$$

forms stout, yellow needles and melts at 181—182°; the *hydrochloride* forms yellow needles and melts at 205°. G. Y.

Action of Alkali Hydroxides and Alkyloxides on Unsaturated Imides.

Arnaldo Piutti (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1906, [iii], **12**, 79—87).—The violet coloration given by *p*-methoxyphenylcitraconimide and other analogous imides (Abstr., 1889, 590) depends on the formation of an additive compound of the alkali or alkaline-earth hydroxide or their alkyloxides or acetonates with the imide itself, a compound which is transformed by moisture into a salt of *p*-methoxyphenylcitraconamic acid. T. H. P.

Preparation of Phenols and their Substitution Products.

Société Chimique des Usines du Rhône (D.R.-P. 167211).—The replacement of a diazonium complex by a hydroxyl group is a reaction which does not always proceed smoothly, and the following process has been found to give favourable results. The solutions of the diazonium salts derived from *o*-anisidine, *o*- and *p*-aminophenols, and *o*-toluidine are introduced into a boiling 50 per cent. solution of copper sulphate. The guaiacol and *o*-cresol produced from *o*-anisidine and *o*-toluidine respectively are distilled in steam, whilst the catechol and quinol obtained from the aminophenols are extracted with ether. From 1·2 to 5 parts of copper sulphate are employed to one of the aromatic amine. G. T. M.

Behaviour of Trinitrobenzene Derivatives with Cyclic Amines. E. O. Sommerhoff (*Zeit. Farb. Ind.*, 1906, 5, 270—271).—In connection with von Georgievics' view that picric acid is capable of existing in two differently coloured forms (this vol., i, 420), it is pointed out that on moistening picric acid with aniline a red colour is first developed which changes to yellow as the ordinary picrate is formed. With dimethylamine in alcoholic solution, picric acid gives the yellow picrate at once, but in benzene solution a transient red coloration is observed. The additive compounds described in conjunction with Noelting (this vol., i, 157) are referred to, and the author is led to dissent from von Georgievics' theoretical views. W. A. D.

***p*-Aminodiphenyl Oxide-3-sulphonic Acid.** Aktiengesellschaft für Anilin-Fabrikation (D.R.-P. 169357).—When *p*-aminodiphenyl oxide is sulphonated with concentrated sulphuric acid at 80—100°, a sulphonic acid is produced containing the sulpho-group in the unsubstituted ring, but when the acid sulphate of *p*-aminodiphenyl oxide is baked at 180° the sulpho-group enters an ortho-position with respect to the amino-group. The new p-*aminodiphenyloxide 3-sulphonic acid* yields valuable lake-forming azo-colouring matters; the free acid and its sodium, calcium, and copper salts are only sparingly soluble in water. G. T. M.

***p*-Hydroxyphenylglycinamide.** Aktiengesellschaft für Anilin-fabrikation (D.R.-P. 166799).—p-*Hydroxyphenylglycinamide*,

$$OH\cdot C_6H_4\cdot NH\cdot CH_2\cdot CO\cdot NH_2,$$

is obtained by condensing chloroacetamide with *p*-aminophenol in the presence of substances capable of fixing hydrogen chloride; an excess of *p*-aminophenol would answer this purpose. For use as a photographic developer, the *p*-hydroxyphenylglycinamide is dissolved in 200 parts of water containing 5 parts of potassium carbonate and 5 parts of anhydrous sodium sulphite. G. T. M.

Derivatives of 3-Amino-*p*-cresol-5-sulphonic Acid. Kalle & Co. (D.R.-P. 168857).—3-Amino-*p*-cresol-5-sulphonic acid is readily acetylated when dissolved in water and the solution exactly neutralised, and the acetyl derivative when nitrated below 5° with a mixture of concentrated nitric and sulphuric acids yields a well-defined, crystalline nitro-derivative, which is readily hydrolysed on boiling with hydrochloric acid. The nitro-3-amino-*p*-cresol-5-sulphonic acid which is thus obtained in a crystalline condition furnishes an azo-β-naphthol having valuable tinctorial properties. G. T. M.

Preparation of 3-Amino-2-hydroxybenzylamine. Alfred Einhorn (D.R.-P. 167572).—3-Nitro-2-hydroxybenzylamine, when reduced with tin and hydrochloric acid, furnishes 3-amino-2-hydroxybenzylamine; this substance, which is a valuable photographic developer, may also be prepared by reducing benzoyl-3-nitro-2-hydroxybenzylamine to *ω-benzoyl-3-amino-2-hydroxybenzylamine*, a base which crystallises in colourless needles melting at 186°, and then hydrolysing this product with concentrated hydrochloric acid. 3-Amino-2-hydroxybenzylamine furnishes a soluble dihydrochloride crystallising in colourless needles; it develops a violet coloration with ferric chloride, precipitates silver from Tollens' solution, sets free gold from its salts, giving rise to a violet coloration, and forms crystalline platini- and stanni-chlorides.

G. T. M.

Preparation of 4-Chloro-α-naphthol. KALLE & Co. (D.R.-P. 167458).—α-Naphthol is conveniently chlorinated by slowly adding to its cold alkaline solution one molecular proportion of sodium hypochlorite also dissolved in aqueous sodium hydroxide. The addition of dilute acetic or hydrochloric acid liberates 4-chloro-α-naphthol, which first separates as an oil and then solidifies in aggregates of needles. The product after distillation in superheated steam or crystallisation in light petroleum melts at 64—65°, and the yield is extremely good.

G. T. M.

Preparation of Aminoarylacylaminonaphtholsulphonic Acids. GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 170045).—The aminonaphtholsulphonic acids readily react in aqueous solution at moderate temperatures with the chlorides of the nitro- and acetylamino-acids of the aromatic series. Thus sodium 6-amino-α-naphthol-3-sulphonate condenses with *m*-nitrobenzoyl chloride in neutral aqueous solution in the presence of sodium acetate to form the compound $HO\cdot C_{10}H_5(SO_3Na)\cdot NH\cdot CO\cdot C_6H_4\cdot NO_2$, and this substance on reduction gives rise to an amine,

$$HO\cdot C_{10}H_5(SO_3Na)\cdot NH\cdot CO\cdot C_6H_4\cdot NH_2,$$

which combines with diazonium salts to produce azo-colouring matters capable of being again diazotised and condensed on the fibre. Similarly, sodium 6-amino-α-naphthol-3-sulphonate combines with acetylaminobenzoyl and benzenesulphonic chlorides, and the products when hydrolysed also give rise to aminosulphonic acids which are used in the production of ingrain azo-dyes. G. T. M.

Condensation Products of α-Naphthol and Benzophenone Chloride. ALBERT G. SHRIMPTON (*Chem. News*, 1906, **94**, 13—14. Compare McKenzie, Trans., 1896, **69**, 985; 1901, **79**, 1204).—*Diphenyldihydroxydi-α-naphthylmethane*, $CPh_2(C_{10}H_6\cdot OH)_2$, obtained when benzophenone chloride is heated with α-naphthol, forms microscopic crystals which darken at 204°, and ultimately melt to a brown, viscid liquid at 208·2—209·2°. When heated with sodium acetate and acetic anhydride in a reflux apparatus, it yields small, silky-white needles and plates melting at 202°, of uncertain composition. When the reaction between α-naphthol and benzophenone chloride is moderated by the presence of a considerable amount of light petroleum, a product is obtained which, when recrystallised from acetone, forms slender, yellow, microscopic prisms melting at 180·5—181°.

D. A. L.

Di*iso*apiole, Di*iso*eugenol Methyl Ether, and Diasarone. Tibor Széki (*Ber.*, 1906, **39**, 2422—2424. Compare Tiemann, Abstr., 1892, 45; Angeli and Mola, Abstr., 1895, i, 24).—*Diisoapiole*, $C_{21}H_{28}O_8$, prepared by treating *iso*apiole with hydrogen chloride in ethereal solution, evaporating off the ether, and heating the residual oil at 200° in a sealed tube, forms white crystals and melts at 97°.

Diisoeugenol methyl ether, $C_{22}H_{28}O_4$, formed by the action of hydrogen chloride on *iso*eugenol methyl ether in ethereal solution, crystallises in snow-white, glistening needles and melts at 106°.

Diasarone, $C_{24}H_{32}O_6$, formed in the same way from asarone, crystallises from alcohol in white needles and melts at 100°.

These three polymerisation products are readily soluble in the usual solvents, and do not form additive compounds with bromine.

In one experiment the diasarone was accompanied by s-*di-trimethoxyphenylethylene*, $C_2H_2[C_6H_2(OMe)_3]_2$, which forms white crystals, melts at 96°, and forms an *additive* compound with bromine.

G. Y.

Derivatives of Asarone. Tibor Széki (*Ber.*, 1906, **39**, 2419—2421).—*Dihydroasarone*, $C_6H_2Pr^{a}(OMe)_3$, prepared by reducing asarone with sodium in alcoholic solution, is obtained as an aromatic, colourless oil, which boils at 185—188° under 40 mm. pressure, and is miscible with alcohol, ether, benzene, or glacial acetic acid.

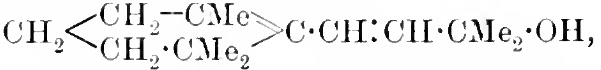
Asarone dibromide (Rizza and Butleroff, Abstr., 1884, 1042), prepared by the action of bromine on asarone in carbon disulphide solution, melts at 83°, and when boiled with sodium ethoxide in alcoholic solution, yields an impure oil having an unpleasant odour. When treated with mercuric oxide and iodine in cooled alcoholic solution, asarone yields α-2 : 4 : 5-*trimethoxyphenylpropaldehyde*,

$$C_6H_2(OMe)_3{\cdot}CHMe{\cdot}CHO,$$

which is an oil boiling at 275° under the ordinary pressure.

G. Y.

Preparation of Tertiary Alcohols. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 166898, 166899).—By the action of excess of organic magnesium haloids ($MgRBr,Et_2O$) on the carboxylic acids or their metallic salts, additive products are obtained, which on treatment with water or acid give rise to a tertiary alcohol. Thus the ethereal solutions of magnesium ethyl bromide and benzoic acid when slowly mixed in the cold evolve ethane and give a precipitate which dissolves completely in dilute ice-cold sulphuric acid. The ethereal extract of this solution furnishes phenyldiethylcarbinol, $CEt_2Ph{\cdot}OH$, which boils at 110° under 12 mm. pressure. *cyclo*Citrylideneacetic acid, when treated in this way with magnesium methyl bromide, ultimately yields the *carbinol*,



$$CH_2{<}\begin{matrix}CH_2{-}CMe\\CH_2{\cdot}CMe_2\end{matrix}{>}C{\cdot}CH{:}CH{\cdot}CMe_2{\cdot}OH,$$

which boils at 130° under 12 mm. pressure; methane is evolved during the initial stage of the reaction. In this operation dry sodium *cyclo*citrylideneacetate may be substituted for the free acid, and in a similar manner anhydrous sodium benzoate may be employed in the preparation of phenyldiethylcarbinol.

G. T. M.

Preparation of *p*-Dialkylaminobenzhydrylamines. EMANUEL MERCK (D.R.-P. 167053).—The oximes, phenylhydrazones, and semicarbazides of the *p*-dialkylaminobenzophenones ($COPh\cdot C_6H_4\cdot NR_2$), when reduced electrically or in neutral acid or alkaline solution with the help of sodium or sodium amalgam, give rise to the *p*-dialkylaminobenzhydrylamines.

p-*Dimethylaminobenzophenoneoxime* crystallises in colourless prisms melting at 152—154°, and when reduced with sodium and ethyl alcohol yields p-*dimethylaminobenzhydrylamine*,

$$NH_2\cdot CHPh\cdot C_6H_4\cdot NMe_2,$$

which forms colourless, acicular crystals and melts at 82·5°; the *hydrochloride* separates in sparingly soluble leaflets melting at 186—187°.

p-*Diethylaminobenzophenoneoxime* crystallises in colourless needles melting at 175—177°; the corresponding hydrazone is oily.

p-*Diethylaminobenzhydrylamine*, $NH_2\cdot CHPh\cdot C_6H_4\cdot NEt_2$, separates in colourless needles melting at 120—121°; its hydrochloride, which is obtained in voluminous aggregates of needles, is sparingly soluble in cold water. These dialkylaminobenzhydrylamines form a new class of anæsthetics. G. T. M.

Preparation of *p*-Dialkylaminobenzhydrylamines. EMANUEL MERCK (D.R.-P. 167462, 167463).—Dimethylaminobenzhydrylamine may be obtained by heating either dimethylaminobenzhydrol, the ethyl ether of this substance, or diethylaminodiphenylbromomethane with ammonia under pressure at 150—200°; it can also be prepared by heating the last of these three compounds with potassium phthalimide at 180°, and then eliminating phthalic acid from the intermediate product by digestion in an autoclave with aqueous alcoholic ammonia at 140°. G. T. M.

Reduction of Aromatic Carbinols. AUGUST KLAGES (*Ber.*, 1906, 39, 2587—2595).—[With ERNST LAUCK and KARL GIESER.]—The reduction of cinnamyl alcohol by sodium and alcohol yields a mixture of propenylbenzene, CHPh:CHMe, and propylbenzene; the former compound was identified by oxidising it to benzoic acid. α-Phenylallylalcohol (this vol., i, 638), with the same reducing agent, yields a mixture of allylbenzene and propylbenzene, which, after treatment with alcoholic potash at 130°, contains propenylbenzene, identified in the form of its bromide.

α-Phenyl-Δ^α-butene-γ-ol is conveniently obtained by decomposing the reaction product of magnesium methyl bromide and cinnamaldehyde with an ice-cold solution of ammonium chloride. It boils at 131° under 12 mm. pressure, and by reduction with sodium and alcohol yields a mixture of butylbenzene and α-phenyl-Δ^β-butylene.

α-*Phenyl*-Δ^α-*pentene*-γ-*ol*, CHPh:CH·CHEt·OH, obtained like the preceding alcohol from magnesium ethyl bromide, is a colourless oil which boils at 138° under 11·5 mm. pressure, and is reduced by sodium and alcohol to α-phenyl-Δ^β-pentene, $CH_2Ph\cdot CH:CHEt$, a colourless, mobile oil with a peculiar odour, which boils at 80° under 12 mm. pressure, has a sp. gr. 0·8837 at 16°/4°, n_D 1·5059 at 16°, and forms an oily *bromide*, $C_{11}H_{14}Br_2$. When this hydrocarbon is heated with alcoholic potash at 150° for one day it is changed into *α-phenyl-Δ^{α}-pentene*, $CHPh{:}CHPr^{\alpha}$, which boils at 82° under 9 mm. pressure, has a sp. gr. 0·892 at 15°/4°, n_D 1·5139 at 15°, and forms a *bromide*, $C_{11}H_{14}Br_2$, which separates from alcohol in colourless leaflets and melts at 61°.

α-Phenyl-γ-methyl-Δ^{α}-butene-γ-ol, $CHPh{:}CH{\cdot}CMe_2{\cdot}OH$, is obtained by decomposing the reaction product of magnesium methyl bromide and benzylideneacetone with ice and ammonium chloride; it melts at 38·5°, boils at 123—124° under 11 mm pressure, and is reduced by sodium and alcohol to α-phenyl-γ-methyl-Δ^{β}-butylene (Abstr., 1904, i, 569).

α-Phenyl-γ-methyl-Δ^{α}-pentene-γ-ol, $CHPh{:}CH{\cdot}CMeEt{\cdot}OH$, obtained like the preceding alcohol from magnesium ethyl bromide, boils at 124—125° under 11 mm. pressure, and is not reduced by sodium and alcohol.

α-Phenyl-γ-methyl-$\Delta^{\alpha\gamma}$-pentadiene, $CHPh{:}CH{\cdot}CMe{:}CHMe$, obtained by decomposing the reaction product of magnesium ethyl iodide (2 mols.) and benzylideneacetone (1 mol.) with ice and dilute sulphuric acid, boils at 130° under 20 mm. pressure, has a sp. gr. 0·9593 at 19°/4°, n_D 1·5366, and is reduced by sodium and alcohol to *α-phenyl-γ-methyl-Δ^{β}-pentene*, $CH_2Ph{\cdot}CH{:}CMeEt$, a colourless, mobile oil which boils at 119—120° under 20 mm. and at 226° under 749 mm. pressure, has a sp. gr. 0·9014 at 18°/4°, n_D 1·5100, and forms a *nitrosylchloride*, which melts at 151°.

Carbinols of the type $CPh{:}C{\cdot}CHR{\cdot}OH$ (where R = alkyl) are obtained from magnesium alkyl haloids and either phenylpropargylaldehyde or α-bromocinnamaldehyde; in the latter case the intermediate brominated alcohol must be boiled with alcoholic potash.

α-Phenyl-α-butinene-γ-ol, $CPh{:}C{\cdot}CHMe{\cdot}OH$, obtained by the second method, is a colourless oil which boils at 121—122° under 9 mm. pressure, and is reduced by sodium and alcohol to a mixture of Δ^{β}-butenylbenzene and a small quantity of butylbenzene.

α-Phenyl-α-pentinene-γ-ol, $CPh{:}C{\cdot}CHEt{\cdot}OH$, obtained by the first method, boils at 133—134° under 10·5 mm. pressure, has a sp. gr. 1·018 at 15·5°/4°, n_D 1·5570 at 15·5°, and forms a heavy oily *bromide*, $C_{11}H_{12}Br_2$, with hydrogen bromide in glacial acetic acid. When the acetylenic alcohol is prepared by the second method, the intermediate *β-bromo-α-phenyl-Δ^{α}-pentene-γ-ol*, $CHPh{:}CBr{\cdot}CHEt{\cdot}OH$, boils at 146—147° under 11 mm. pressure, has a sp. gr. 1·3533 at 17°/4°, and n_D 1·5840 at 17°. The reduction of the acetylenic alcohol by sodium and alcohol yields the Δ^{β}-pentenylbenzene described above. C. S.

Migration of the Phenyl Group in the Halohydrins and the α-Glycols. Marc Tiffeneau (*Compt. rend.*, 1906, **142**, 1537—1539. Compare Abstr., 1902, i, 666; 1904, i, 63, 133).—ββ-Diphenylethylene glycol, $OH{\cdot}CPh_2{\cdot}CH_2OH$, prepared by the action of magnesium phenyl bromide on ethyl glycollate, is converted quantitatively into diphenylacetaldehyde, $CHPh_2{\cdot}CHO$, by the action of sulphuric acid, and α-phenylpropylene-αβ-glycol, $OH{\cdot}CHPh{\cdot}CHMe{\cdot}OH$ (compare

Zincke, Abstr., 1884, 1003), is converted similarly into phenylacetone, $CH_2Ph\cdot CO\cdot CH_3$.

The transformation of the substituted α-glycols into the corresponding aldehyde or ketone by the action of sulphuric acid does not therefore involve the migration of a phenyl group except in the case of hydrobenzoin, whilst in the similar transformation of the corresponding iodohydrins by means of silver nitrate the change is always accompanied by the migration of a phenyl group. M. A. W.

Cholesterol. II. Specific Rotations of Cholestene and Cholestane Derivatives. Julius Mauthner (*Monatsh.*, 1906, **27**, 421—431. Compare this vol., i, 579; Mauthner and Suida, Abstr., 1894, i, 326, 486; 1896, i, 425; 1897, i, 31; 1903, i, 625; Windaus, Abstr., 1904, i, 49, 667; this vol., i, 174, 579, 580; Diels and Abderhalden, this vol., i, 272).—The author has determined the influence of the addition of halogens and of hydrogen haloids on the specific rotations of cholesterol, cholestene, and cholestane. The substances were dissolved in ether, alcohol, or chloroform.

Cholesterol has $[\alpha]_D$ $-29\cdot92°$, the hydrochloride $[\alpha]_D$ $+5\cdot7°$, the dichloride $[\alpha]_D$ $-29\cdot1°$, and the dibromide $[\alpha]_D$ $-41\cdot6°$. Cholestanonol has $[\alpha]_D$ $-3\cdot14°$.

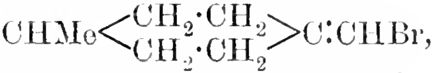
Cholesteryl acetate has $[\alpha]_D$ $-29\cdot8°$, its dichloride $[\alpha]_D$ $-32\cdot8°$, and its dibromide $[\alpha]_D$ $-45\cdot1°$.

Cholesteryl chloride has $[\alpha]_D$ $-26\cdot36°$; the hydrochloride [β-dichlorocholestane] has $[\alpha]_D$ $+20\cdot1°$ in benzene solution or $+12\cdot16°$ in ethereal solution. Trichlorocholestane has $[\alpha]_D$ $-34\cdot7°$. Cholesteryl chloride dibromide, which melts at 130—131°, has $[\alpha]_D$ $-55\cdot0°$.

Cholestene hydrochloride [chlorocholestane] has $[\alpha]_D$ $+21\cdot8°$, and cholestene dichloride [α-dichlorocholestane] $[\alpha]_D$ $-28\cdot7°$.

α-Cholestene dibromide (Mauthner and Suida, Abstr., 1894, i, 326) melts at 145—146° and has $[\alpha]_D$ $+48\cdot9°$. β-Cholestene dibromide immediately after solution in chloroform has $[\alpha]_D$ $-39\cdot6°$, after twenty-four hours $[\alpha]_D$ $\pm 0°$, and at the end of some days $[\alpha]_D$ $+39\cdot4°$. The last specific rotation is not increased beyond $+40°$ on heating the solution in a sealed tube at 65° for one hour, but on evaporation the α-dibromide is obtained. The change in the rotation takes place much more slowly in benzene solution. The dibromocholestanes are probably alicyclic *cis-trans*-isomerides. G. Y.

4-Methyl*cyclo*hexylidene-1-acetic Acid. Willy Marckwald and Richard Meth (*Ber.*, 1906, **39**, 2404—2405. Compare this vol., i, 360, 584).—When treated with bromine in aqueous sodium carbonate solution, 4-methyl*cyclo*hexylidene-1-acetic acid, melting at 40·5—41°, yields 1-*methyl*-4-*bromomethylene*cyclo*hexane*,



$$CHMe{<}\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}{>}C{:}CHBr,$$

which, when heated with water at 140—150°, forms hexahydro-*p*-tolualdehyde (Wallach and Evans, this vol., i, 566). Perkin and Pope's acid melting at 88° (Proc., 1906, **22**, 107) is probably 4-methyl-Δ^1-*cyclo*hexene-1-acetic acid,  $CHMe{<}\begin{matrix}CH_2\text{—}CH\\ CH_2\cdot CH_2\end{matrix}{>}C\cdot CH_2\cdot CO_2H$ (compare Rupe, Ronus, and Lotz, Abstr., 1903, i, 139). G. Y.

Conversion of Aldoximes into Nitriles. WALTHER BORSCHE (*Ber.*, 1906, **39**, 2503).—If 2 mols. of an aldoxime are heated with 1 mol. of lead oxide, the lead derivative of the aldoxime,

$$(R\cdot CH\colon NO)_2Pb,$$

is formed, and on further heating is decomposed into lead oxide, water, and the nitrile. The violence of the action is moderated by mixing the reacting substances with an amount of sand two to three times the weight of the aldoxime. Nitriles have been prepared in this manner from benzaldoxime, anisaldoxime, cuminaldoxime, heptaldoxime, and furfuraldoxime. G. Y.

Crystallographic Study of New Organic Compounds. FRANCESCO RANFALDI (*Atti R. Accad. Lincei*, 1906, [v], **15**, i, 715—724).— Sodium 2-*o*-nitro-*p*-toluidino-3 : 5-dinitrobenzoate (Cuttitta, *Rend. Soc. Chim. Roma*, 1905, 146) crystallises in the triclinic system [$a:b:c = 1·52579:1:0·94494$; $\alpha = 76°11'$, $\beta = 81°27'$, $\gamma = 93°29'$].

The corresponding pyridine salt (Cuttitta, *loc. cit.*) crystallises in the triclinic system [$a:b:c = 1·35414:1:1·09430$; $\alpha = 87°16'$, $\beta = 76°36'$, $\gamma = 92°14'6''$].

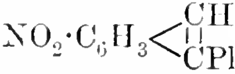
i-Lupanine platinichloride (Soldaini, Abstr., 1892, 892) crystallises in the monoclinic system [$a:b:c = 2·6124:1:1·3428$; $\beta = 83°46'33''$].

Ethyl naphthalate (Errera), $C_{10}H_6(CO_2Et)_2$, melting at 58—60°, crystallises in the monoclinic system [$a:b:c = 1·0555:1:3·1814$; $\beta = 70°45'27''$]. T. H. P.

Products of Dehydration of Phenyl-*o*-nitrocinnamic Acid and the Products which accompany this Acid when prepared by Perkin's Synthesis. MARUSSIA BAKUNIN and L. PARLATI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1906, [iii], **12**, 18—34).—When sodium phenylacetate, *o*-nitrobenzaldehyde, and acetic anhydride are heated at 120°, α-phenyl-*o*-nitrocinnamic acid is formed and less resin is obtained than at 160°. The portion of the product insoluble in sodium carbonate solution contains: (1) o-*nitrobenzylidene diacetate*,

$$NO_2\cdot C_6H_4\cdot CH(OAc)_2,$$

which crystallises from light petroleum in small, yellow prisms melting at 89—90°, dissolves in most solvents, and is slightly decomposed by a solution of phenylhydrazine, giving *o*-nitrobenzaldehyde phenylhydrazone; (2) *phenyl*-o-*nitrophenylacrylene* (?) [*phenyl*-o-*nitrophenylenethylene*],



$NO_2\cdot C_6H_3{<}\begin{matrix}CH\\ \|\\ CPh\end{matrix}$, which crystallises from ethyl acetate in ruby-red, shining, rhombic laminæ

$$[a:b:c = 0·68275:1:1·04489]$$

and melts at 186—187°.

Ethyl phenyl-o-*nitrocinnamate*, obtained by the action of alcohol on the acid, separates from light petroleum in yellow, monoclinic prisms melting at 59° and is soluble in alcohol.

Phenylhydrazine phenyl-o-*nitrocinnamate*, $C_{15}H_{11}O_4N,NHPh\cdot NH_2$, crystallises from benzene in tufts of silky, yellow, unstable needles and melts at 97—103°.

Phenyl-o-nitrocinnamoyl phenylhydrazide, $C_{21}H_{17}O_3N_3$, prepared by the action of excess of phenylhydrazine on phenyl-*o*-nitrocinnamic anhydride, crystallises from alcohol in shining, yellow laminæ melting at 167°. It is accompanied by a small quantity of a yellow powder, infusible at 300°, the nature of which has not been determined.

Phenyl-o-nitroindone phenylhydrazone, $C_{15}H_9O_2N{:}N_2HPh$, crystallises from benzene in canary-yellow, silky needles melting at 135—136°. The *oxime*, $C_{15}H_{10}O_2N{:}NOH$, crystallises from benzene in silky, orange-yellow needles melting at 246—248°. T. H. P.

Action of Sodium Hypochlorite and of Bromine and Sodium Alkyloxides on Hydrocinnamamide. R. A. Weermann and W. J. A. Jongkees (*Rec. trav. chim.*, 1906, **25**, 238—243).—Hydrocinnamamide (1 mol.) reacts with sodium hypochlorite (1 mol.) and sodium hydroxide ($\frac{1}{2}$ mol.) at the ordinary temperature to form *s*-β-diphenylethylcarbamide; if, however, the quantity of sodium hydroxide is increased and the temperature is raised to 80°, β-diphenylethylamine is obtained.

Hydrocinnamamide reacts with bromine and sodium ethoxide or methoxide at the boiling point of the alcohol to form the corresponding alkyl ester of β-phenylethylaminoformic acid; ethyl benzylaminoformate, similarly prepared from phenylacetamide, melts at 44°, and *methyl benzylaminoformate* crystallises in thin needles from light petroleum and melts at 64—65°. M. A. W.

Formation of Salicylic Acid from Sodium Phenoxide. Jacob Moll van Charante (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, **9**, 20—23).—On heating sodium phenyl carbonate in a sealed tube at 100°, carbon dioxide and phenol are formed along with small amounts of sodium salicylate. Sodium phenoxide crystallises from acetone with 1 mol. of the solvent in long, soft, and almost white needles. When sodium phenyl carbonate is placed in dry acetone, it yields carbon dioxide, phenol, and a mixture of normal and acid sodium carbonates. Sodium salicylate crystallises from acetone in small needles containing $\frac{1}{2}$ to 1 mol. of the solvent, whereas disodium salicylate is insoluble in acetone. E. F. A.

Bismuth Disalicylate. Chemische Fabrik von Heyden, Aktien-Gesellschaft (D.R.-P. 168408).—The "*bismuthum salicylicum basicum*" or "*bismuthum subsalicylicum*" of commerce is the monosalicylate of bismuth having the formula $OH{\cdot}C_6H_4{\cdot}CO{\cdot}O{\cdot}BiO$. The so-called neutral bismuth salicylate is a mixture of a basic salt and free salicylic acid. *Bismuth disalicylate*, $OH{\cdot}Bi(O{\cdot}CO{\cdot}C_6H_4{\cdot}OH)_2$ or $O[Bi(O{\cdot}CO{\cdot}C_6H_4{\cdot}OH)_2]_2$, has now been prepared by adding crystallised bismuth nitrate to an aqueous solution of sodium salicylate, and, after thorough mixing, extracting the free salicylic acid at the ordinary temperature with either dilute ammonia or indifferent solvents such as alcohol, ether, or chloroform. The product is a white, almost tasteless powder, which has a neutral reaction in cold water, but is decomposed on warming into the monosalicylate and free salicylic acid.

G. T. M.

Action of Chloroform and Sodium Hydroxide on Phenols in Acetone Solution.

GUIDO BARGELLINI (*Atti R. Accad. Lincei*, 1906, [v], **15**, i, 579—587).—The compound, $C_{10}H_{12}O_3$, which was obtained by Link (D.R.-P. 80986) by heating an acetone solution of phenol with chloroform and sodium hydroxide, and was regarded by this author as hydroxyphenyl hydroxy*iso*propyl ketone or hydroxy*iso*butyrylphenol, $OH\cdot C_6H_4\cdot CO\cdot CMe_2\cdot OH$, exhibits none of the reactions of phenols or ketones, whilst it contains a carboxyl group; it must hence be assumed to be α-phenoxy*iso*butyric acid, $OPh\cdot CMe_2\cdot CO_2H$, and it agrees in properties with the data given by Bischoff (Abstr., 1900, i, 345) for this compound. The corresponding naphthol derivatives described by Link are identical with the α- and β-naphthoxy*iso*butyric acids prepared by Bischoff (Abstr., 1900, i, 395).

By the action of chloroform, sodium hydroxide, and acetone on *o*- or *p*-cresol or thymol, the author has obtained compounds identical with those prepared by Bischoff (Abstr., 1900, i, 392 and 394) by the action of ethyl α-bromo*iso*butyrate on the sodium derivatives of *o*- or *m*-cresol or thymol.

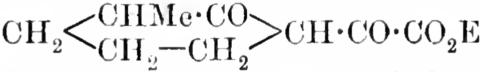
The views of Link concerning these compounds (compare Beilstein, Handbuch, III, Suppl., 120 and 143) are hence erroneous.

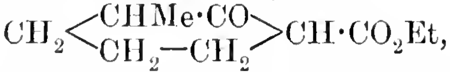
The first phase in the reaction is probably the formation of acetone-chloroform (which may, indeed, be used in place of the chloroform), this being then acted on by sodium hydroxide in presence of acetone, yielding α-hydroxy*iso*butyric acid, which, with the phenol, gives α-phenoxy*iso*butyric acid. The chloroform may also be replaced by bromoform, bromal, chloral, or carbon tetrachloride or tetrabromide.

The compounds prepared by the author have all been described previously.

T. H. P.

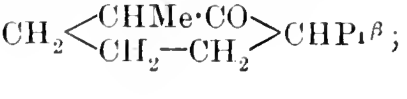
Syntheses by means of the Carboxylic Esters of Cyclic Ketones. II. Synthesis of *m*-Menthane-2-one and of *m*-Menthane-4-one from 1-Methyl*cyclo*hexane-2-one and 1-Methyl*cyclo*hexane-4-one.

ARTHUR KÖTZ and A. MICHELS (*Annalen*, 1906, **348**, 91—96. Compare Kötz and Hesse, this vol., i, 88).—When distilled under reduced pressure, *ethyl 3-methyl*cyclo*hexane-2-one-1-oxalate*,  $CH_2<\begin{matrix}CHMe\cdot CO\\ CH_2-CH_2\end{matrix}>CH\cdot CO\cdot CO_2Et$, prepared by the action of ethyl oxalate and sodium on 1-methyl*cyclo*hexane-2-one in presence of light petroleum, loses carbon monoxide and yields *ethyl 3-methyl*cyclo*hexane-2-one-1-carboxylate*,



$$CH_2<\begin{matrix}CHMe\cdot CO\\ CH_2-CH_2\end{matrix}>CH\cdot CO_2Et,$$

which boils at 115° under 12 mm. pressure and forms a *semicarbazone*, $C_{11}H_{19}O_3N_3$, melting at 140°. With *iso*propyl iodide and sodium ethoxide it forms *ethyl 3-methyl-1-*iso*propyl*cyclo*hexane-2-one-1-carboxylate*, $C_6H_7OMePr^{\beta}\cdot CO_2Et$, which boils at 128° under 10 mm. pressure, forms a *semicarbazone* only slowly, and on hydrolysis and elimination of carbon dioxide yields m-*menthane-2-one*,

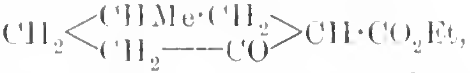


$$CH_2<\begin{matrix}CHMe\cdot CO\\ CH_2-CH_2\end{matrix}>CHPr^{\beta};$$

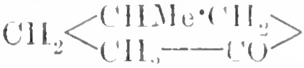
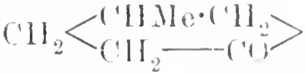
this boils at 82° under 10 mm. pressure, has a sp. gr. 0·9128 at 15°, and reacts slowly with semicarbazide.

The following substances have been prepared in the same manner, starting from 1-methyl*cyclo*hexane-4-one.

*Ethyl 3-methyl*cyclo*hexane-6-one-1 carboxylate*,



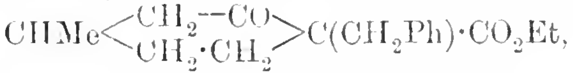
$$CH_2<\substack{CHMe\cdot CH_2\\CH_2 — CO}>CH\cdot CO_2Et,$$

boils at 110° under 10 mm. pressure and forms a *semicarbazone*, $C_{11}H_{19}O_3N_3$, melting at 134°. *Ethyl 3 methyl*-1-iso*propyl*cyclo*hexane-6-one*-1-*carboxylate*,  $CH_2<\substack{CHMe\cdot CH_2\\CH_2 — CO}>CPr^{\beta}\cdot CO_2Et$, boils at 125—127° under 10 mm. pressure and forms a *semicarbazone*, $C_{11}H_{25}O_3N_3$, melting at 130°. m-*Menthane-4-one*,  $CH_2<\substack{CHMe\cdot CH_2\\CH_2 — CO}>CHPr^{\beta}$, boils at 195°, has a sp. gr. 0·8914 at 15°, and forms an *oxime*, $C_{10}H_{19}ON$, melting at 105°.

G. Y.

Syntheses by means of the Carboxylic Esters of Cyclic Ketones. III. Dicyclic Systems of indirectly connected Six-atom Rings. ARTHUR KÖTZ and GUSTAV KAYSER (*Annalen*, 1906, **348**, 97—110. Compare Kötz and Hesse, this vol., i, 88; Kötz and Michels, preceding abstract).—The substances described in this paper were prepared by the action of the haloid compounds mentioned and sodium ethoxide on ethyl 4-methyl*cyclo*hexane-2-one-1-carboxylate in absolute alcoholic solution.

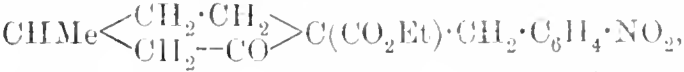
*Ethyl 1-benzyl-4-methyl*cyclo*hexane-2-one-1-carboxylate*,



$$CHMe<\substack{CH_2 — CO\\CH_2\cdot CH_2}>C(CH_2Ph)\cdot CO_2Et,$$

from benzyl chloride, distils at 194° under 12 mm. pressure. The *semicarbazone*, $C_{18}H_{25}O_3N_3$, melts at 169°. When boiled with methyl-alcoholic potassium hydroxide, the ester yields *4-benzyl-1-methyl*cyclo*hexane-3-one*, $C_6H_8OMe\cdot CH_2Ph$, which is colourless and boils at 166° under 10 mm. or at 173° under 13 mm. pressure; the *semicarbazone*, $C_{15}H_{21}ON_3$, melts at 172°; the *oxime*, $C_{14}H_{19}ON$, melts at 139°.

*Ethyl 1-p-nitrobenzyl-4-methyl*cyclo*hexane-2-one-1-carboxylate*,



$$CHMe<\substack{CH_2\cdot CH_2\\CH_2 — CO}>C(CO_2Et)\cdot CH_2\cdot C_6H_4\cdot NO_2,$$

from *p* nitrobenzyl chloride, crystallises in glistening, golden-yellow needles and melts at 90·5°.

The action of phenacyl bromide on ethyl 4-methyl*cyclo*hexane-2 one-1-carboxylate and sodium ethoxide leads to the formation of bromodiphenacyl.

Ethyl βκ-dimethylundecane-αεηλ-tetracarboxylate,

$$CH_2[CH(CO_2Et)\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH_2\cdot CO_2Et]_2,$$

formed from methylene iodide, is obtained as a viscid oil boiling at 253° under 16 mm. pressure.

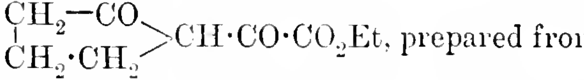
Only a small amount of ethyl β-methylpimelate is obtained from ethylene bromide, most of the ketone-ester being regained unchanged.

*Ethyl 4 : 4'-dimethyl-1 : 1'-trimethylene*di*cyclo*hexane-2 : 2'-dione-1 : 1'-dicarboxylate*, $C_3H_6(C_6H_7OMe\cdot CO_2Et)_2$, formed from trimethylene dibromide, is obtained as a viscid oil which boils at 257—263° under

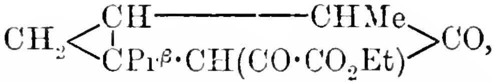
18 mm. pressure and is converted by the action of sodium ethoxide into *ethyl βμ-dimethyltridecane-αεν-tetracarboxylate*,

$CH_2[CH_2\cdot CH(CO_2Et)\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH_2\cdot CO_2Et]_2$;

this forms a yellow oil boiling at 287—294° under 14 mm. pressure. When boiled with methyl-alcoholic potassium hydroxide, the dicarboxylate is hydrolysed, and decomposes, forming 1 : 1′-*dimethyl*-4 : 4′-*trimethylenedicyclohexane*-3 : 3′-*one* ; this forms a *semicarbazone*, $C_{19}H_{21}O_2N_6$, which melts at 107° and on treatment with sulphuric acid yields a small amount of a colourless *oil* boiling at about 204°. G. Y.

αγ-Diketocarboxylic Esters of the *cyclo*Pentane and Bi*cyclo*-(0 : 1 : 3)-hexane Groups. Arthur Kötz, Arthur Bieber, and P. Schüler (*Annalen*, 1906, **348**, 111—119).—*Ethyl* cyclo*pentane*-2-*one*-1-*oxalate*,  $\begin{matrix}CH_2-CO\\ |\\ CH_2\cdot CH_2\end{matrix}\!>CH\cdot CO\cdot CO_2Et$, prepared from *cyclo*pentane-2-one, ethyl oxalate, and sodium ethoxide in cooled absolute alcoholic solution, forms a colourless oil which boils at 138—139° under 14 mm. pressure, gives a brown coloration with ferric chloride, and forms a *semicarbazone.* It resinifies when boiled under the ordinary pressure or when heated with dilute sulphuric acid, yields oxalic acid when boiled with dilute sodium hydroxide, and is partially decomposed at 150° in a sealed tube.

Ethyl 3 : 4-*dimethyl*-2-iso*propylcyclopentene*-5-*one*-1-*oxalate* (*ethyl* iso*thujoneoxalate*),  $\begin{matrix}CMe-\!\!-\!\!-CO\\ \|\\ CMe\cdot CHPr^{\beta}\end{matrix}\!>CH\cdot CO\cdot CO_2Et$, prepared by acting with sodium ethoxide on *iso*thujone and ethyl oxalate in cooled absolute alcoholic solution, boils at 182—184° under 11 mm. pressure, and when distilled under the ordinary pressure yields *iso*thujone and a small amount of *ethyl* iso*thujonecarboxylate*, $C_{13}H_{20}O_3$, which boils at 169° under 11 mm. pressure and gives a blue coloration with ferric chloride. The *semicarbazone* of ethyl *iso*thujoneoxalate, $C_{15}H_{23}O_4N_3$, melts at 168—169°.

Ethyl thujoneoxalate,  $CH_2\!<\!\begin{matrix}CH-\!\!-\!\!-\!\!-\!\!-\!\!-CHMe\\ |\\ CPr^{\beta}\cdot CH(CO\cdot CO_2Et)\end{matrix}\!>CO$, formed in similar manner to the *iso*-ester, boils at 168—170° under 11 mm. pressure ; the *semicarbazone*, $C_{15}H_{23}O_4N_3$, melts at 156—157°. When boiled under the ordinary pressure for two days, the ester yields a mixture of thujone and *ethyl thujonecarboxylate*, $C_{13}H_{20}O_3$, which gives a violet coloration with ferric chloride. A similar mixture is obtained by heating the ethyl oxalate under pressure at 220°. On prolonged heating with dilute sulphuric acid, the ethyl oxalate yields oxalic acid, thujone, and *iso*thujone, whilst with concentrated hydrochloric acid at 125° oxalic acid, carbon monoxide and dioxide, and *iso*thujone are formed.

The behaviour, when heated under the ordinary pressure, of the product formed with sodium ethoxide and ethyl oxalate may be used to determine whether the group $-CH_2\cdot CO$ is present in a five- or six-atom ring. G. Y.

Benzoylsalicylic [*o*-Benzoyloxybenzoic] Acid. F. HOFFMANN, LA ROCHE & Co. (D.R.-P. 169247).—*o-Benzoyloxybenzoic acid*, $OBz{\cdot}C_6H_4{\cdot}CO_2H$, and its salts have not hitherto been obtained, but the acid is prepared readily by treating disodium salicylate at low temperatures with 1 mol. or slight excess of benzoyl chloride diluted with petroleum or ether. The residue after pouring off the diluent is extracted with water and the *o*-benzoyloxybenzoic acid precipitated with acid and recrystallised from dilute alcohol. It is quite insoluble in cold water, dissolving sparingly on warming; it dissolves readily in ether, alcohol, or chloroform and does not give the reactions of salicylic acid until after hydrolysis with alkalis. The crystalline acid melts at 132°. G. T. M.

Reduction of $\alpha\beta$-Unsaturated Carboxylic Esters with Aluminium Amalgam. FRANZ HENLE (*Annalen*, 1906, **348**, 16—30. Compare Thiele and Buchner, this vol., i, 569; Harries and Eschenbach, Abstr., 1896, i, 305; H. Wislicenus, Abstr., 1896, i, 672).—Methyl cinnamate is reduced by aluminium amalgam and water in ethereal solution in four to six days, forming methyl dihydrocinnamate in a yield of 55—65 per cent., methyl $\beta\gamma$-diphenyladipate in a yield of 8—9 per cent., and an isomeride of the latter melting at 73° in a yield of 4—5 per cent.

Methyl $\beta\gamma$-diphenyladipate, $CO_2Me{\cdot}CH_2{\cdot}CHPh{\cdot}CHPh{\cdot}CH_2{\cdot}CO_2Me$, crystallises from ethyl acetate, melts at 175°, is sparingly soluble in hot ether, alcohol, or light petroleum, but readily so in other hot organic solvents, does not decolorise potassium permanganate or bromine, and on hydrolysis yields *$\beta\gamma$-diphenyladipic acid*,

$$C_{18}H_{18}O_4,C_2H_6O,$$

which crystallises from alcohol in small, glistening, colourless prisms, loses C_2H_6O at 105°, melts at about 270°, is insoluble in water, reddens moist litmus paper in alcoholic solution, and dissolves in aqueous sodium carbonate. When fused with potassium hydroxide, the acid is oxidised, forming benzoic and acetic acids. *$\beta\gamma$-Diphenyladipic diacetic anhydride*, $C_4H_6Ph_2(CO{\cdot}OAc)_2$, formed by boiling the acid with acetyl chloride in a reflux apparatus, crystallises from light petroleum, melts at 100—105°, resolidifies on further heating, and melts again to a yellow liquid at 235—240°. It is soluble in chloroform, loses acetic anhydride slowly in a vacuum, quickly at 140°, forming a brown, granular mass, which is not the adipic anhydride, melts at 225—240°, and is soluble in boiling nitrobenzene. The mixed anhydride is hydrolysed by boiling water, forming acetic and $\beta\gamma$-diphenyladipic acids. A white *substance*, only sparingly soluble in chloroform and insoluble in aqueous sodium carbonate, is formed together with the mixed anhydride by the action of freshly-distilled acetyl chloride on $\beta\gamma$-diphenyladipic acid.

The *isomeride* of methyl $\beta\gamma$-diphenyladipate, $C_{20}H_{22}O_4$, melting at 73°, crystallises from hot light petroleum, is readily soluble in other organic solvents, and behaves as a saturated ester towards potassium permanganate and bromine. The *acid*, $C_{18}H_{18}O_4$, crystallises from water, melts at 169—170°, has an acid reaction in aqueous solution, and is probably a stereoisomeride of the $\beta\gamma$-diphenyladipic acid melting at 270°.

Ethyl benzylmalonate is obtained in a 60 per cent. yield by the reduction of ethyl benzylidenemalonate with aluminium amalgam and moist ether. Ethyl cinnamylidenemalonate also is reduced by aluminium amalgam and moist ether. G. Y.

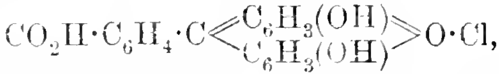
Constitution of the Phenolphthalein and Quinolphthalein Salts. ARTHUR G. GREEN and PERCY E. KING (*Ber.*, 1906, **39**, 2365—2371).—A reply to Meyer and Spengler's criticism (Abstr., 1905, i, 440) of the views of Green and Perkin (Trans., 1904, **85**, 398). The following facts prove the existence of coloured quinonoid alkyl esters of the phthaleins, such as $O{:}C_6H_4{:}C(C_6H_4\cdot OH)\cdot C_6H_4\cdot CO_2Me$, and hence support the contention that the coloured alkali salts of the phthaleins have the analogous structure,

$$O{:}C_6H_4{:}C(C_6H_4\cdot OH)\cdot C_6H_4\cdot CO_2Na.$$

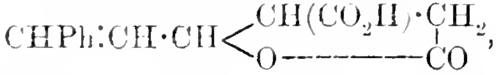
The analogy between the phthaleins and the fluoresceins, assumed in the previous paper, is thus made complete; the apparent differences between the two series are in reality merely differences of stability.

The *ester*, $O{:}C_6H_4{:}C(C_6H_4\cdot OH)\cdot C_6H_4\cdot CO_2Me$, prepared by saturating a methyl-alcoholic solution of phenolphthalein containing zinc chloride with hydrogen chloride, and subsequently pouring the solution into ice-cold water, forms a scarlet-red precipitate, which is rapidly hydrolysed by water at the ordinary temperature, becoming colourless; even when dried in a desiccator, partial hydrolysis takes place, the colour changing from dark red to rose-red. The same red salt is apparently formed on heating phenolphthalein with methyl sulphate, giving a red solution, but it has not yet been isolated.

On passing hydrogen chloride through a solution of quinolphthalein in methyl alcohol, small, red crystals of the *chloride* of the *quinonoid methyl ester*,  $CO_2Me\cdot C_6H_4\cdot C{<}\begin{array}{c}C_6H_3(OH)\\C_6H_3(OH)\end{array}{>}O\cdot Cl$, separate; this substance is stable when dry and is much less easily decomposed by water than the quinonoid ester of phenolphthalein. When heated with aqueous alkalis it is, however, rapidly converted into the ordinary violet salts of quinolphthalein.

The *chloride*,  $CO_2H\cdot C_6H_4\cdot C{<}\begin{array}{c}C_6H_3(OH)\\C_6H_3(OH)\end{array}{>}O\cdot Cl$, of quinolphthalein, prepared by passing hydrogen chloride into a warm solution of the phthalein in glacial acetic acid, also forms red crystals; it is decomposed instantaneously by water, alcohol, or by ether containing alcohol. W. A. D.

Cinnamenylparaconic Acid. J. BOUGAULT (*Compt. rend.*, 1906, 142, 1539—1541).—*Cinnamenylparaconic acid*,



$$CHPh{:}CH\cdot CH{<}\begin{array}{l}CH(CO_2H)\cdot CH_2\\O\text{---------}CO\end{array},$$

prepared by the action of cinnamaldehyde on sodium succinate in the presence of acetic anhydride, melts at 145°, is very sparingly soluble in water, benzene, or light petroleum, sparingly soluble in ether or chloroform, a little more so in cold alcohol (0·5 to 0·6 per cent.), much more soluble in hot alcohol; it is reprecipitated immediately by a strong acid from solution in sodium carbonate, but only after several hours from solution in sodium hydroxide; the *dibromide* is crystalline, and melts and decomposes at 205°; it is very sparingly soluble in the ordinary solvents, dissolves readily in sodium carbonate, but when the solution is heated decomposition ensues with the formation of sodium bromide, benzaldehyde, and other products not yet examined.

Cinnamenylparaconic acid is readily converted by the action of boiling water into cinnamenyl*iso*crotonic acid, which was the only product obtained by Fittig and Batt (Abstr., 1904, i, 744), who first examined the action of cinnamaldehyde on sodium succinate. M. A. W.

Salts of Mineral Acids derived from the Phthaleins. I. Gustav Heller [and, in part, Otto Langkopf] (*Zeit. Farb. Ind.*, 1906, 5, 265—269).—*Gallein hydrochloride alcoholate*, $C_{20}H_{12}O_7,HCl,C_2H_6O$, prepared by dissolving gallein in alcoholic hydrochloric acid, crystallises in brown prisms or plates. The corresponding *acetone* derivative, $C_{20}H_{12}O_7,HCl,C_3H_6O$, obtained from gallein, hydrochloric acid, and acetone, forms bluish-black needles. The formation of these substances can be utilised in purifying gallein. Pure gallein, obtained by decomposing either of the above compounds with concentrated sulphuric acid and adding water to the filtered solution, differs from ordinary gallein by giving only a slight yellowish-red coloration when dissolved in alcohol or acetone. *Gallein hydrochloride methyl alcoholate*, $C_{20}H_{12}O_7,HCl,MeOH$, crystallises from methyl alcohol on adding ether in clusters of needles. *Gallein sulphate*, $C_{20}H_{12}O_7,H_2SO_4$, does not crystallise with alcohol or acetone. The *hydrobromide*, however, like the hydrochloride, crystallises from acetone with 1 mol. of the solvent.

Gallein ethyl ester gives with hydrochloric acid in presence of either alcohol or acetone the *hydrochloride*, $C_{22}H_{16}O_7,HCl$, which forms brownish-red needles and does not crystallise with the solvent. The analogous *sulphate*, $C_{22}H_{16}O_7,H_2SO_4$, is similar.

All the foregoing salts of gallein are decomposed by cold water. On adding an alcoholic solution of any one of them to boiling water, the reddish-brown *gallein hydrate*, $C_{20}H_{12}O_7,H_2O$, separates as a crystalline powder which loses $1H_2O$ at 180°. A second modification of this substance, having a bluish-violet colour when dried in a vacuum, is obtained by adding the alcoholic solution of the salt to cold water, or by decomposing by a mineral acid the salts formed by gallein with alkalis. A third hydrated form is obtained as a blackish-red, crystalline powder on adding chloroform to a solution of pure gallein in acetone or by decomposing an alkali salt of gallein with acetic acid. Anhydrous gallein, obtained by expelling water from the hydrated forms or by fusing phthalic anhydride with pyrogallol, forms nearly black crystals. The relationship between the foregoing substances will be discussed in a subsequent paper. The alkali salts of gallein also exist in two modifications. The salt obtained by dissolving gallein in alkali is intensely violet; a red *potassium* salt, $C_{20}H_{11}O_7K$, is, however, formed on mixing alcoholic solutions of gallein and of potassium acetate.

Hydroxyquinolphthalein (Feuerstein and Dutoit, Abstr., 1901, i, 723) gives salts similar to those of gallein; the *hydrochloride ethyl* *alcoholate*, *methyl alcoholate*, and *acetonate* are described. The *sulphate*, $C_{20}H_{12}O_7,H_2SO_4$, does not crystallise with the solvent.

Cœrulein *hydrochloride* and *sulphate* were prepared; these salts contain only about three-fourths of the amount of acid calculated for the formulæ $C_{20}H_{10}O_6,HCl$ and $C_{20}H_{10}O_6,H_2SO_4$ respectively. W. A. D.

Compounds from Lichens. XV. Wilhelm Zopf (*Annalen*, 1906, 346, 82—127. Compare Abstr., 1905, i, 212, 789).—The lichen, *Rhizoplaca chrysoleuca*, Zopf (*Lecanora chrysoleuca*, Ach; *Squamaria chrysoleuca*, or *Placodium chrysoleucum*), contains usnic acid and placodiolin, or, better, *placodiolic acid*, $C_{17}H_{18}O_7$, the latter of which dissolves when the plant is extracted with sodium hydrogen carbonate. It is precipitated from the solution with acid, and crystallises in leaflets or monoclinic, yellowish-green plates, melting at 156—157°; in chloroform solution it has $[\alpha]_D - 238°$ at 17°; its mol. weight was determined in acetone and cryoscopically in benzene, and found to be 315·6 in the one and 306 in the other solvent. In alkaline solution, the acid reduces potassium permanganate.

The usnic acid obtained from *Rhizoplaca opaca*, Zopf, has $[\alpha]_D - 482{\cdot}3°$ at 22°, and was converted into Widman's decarbousnic acid melting at 176°.

Contrary to previous statements, neither zeorin nor sordidin was found in *Lecanora sulphurea*, but a crystalline *substance* melting at 100° was found together with usnic acid. It would appear that two modifications of this lichen exist, distinct in their chemical characters.

It is suggested that the rhizocarpinic acid melting at 170° described by Hesse is impure rhizocarpic acid which melts at 177—179°.

Biatora Lightfootii contains at least 6 per cent. of *l*-usnic acid ($[\alpha]_D - 455{\cdot}9°$), to which is ascribed the yellowish- or greyish-green colour of the thallus. A colourless, crystalline compound is also present in small quantities.

The lichen, *Biatora granulosa* (*Lecidea granulosa* var. *decolorans*, *Patellaria decolorans*), contains gyrophoric acid melting at 202—203°, which, when heated with alcohol in a closed tube, yields ethyl orsellate melting at 132°. The presence of paretin is probably the cause of the violet colour which extracts of *Blastenia Jungermanniæ* give with alkali hydroxides.

Diploschistessic acid, $C_{15}H_{16}O_7$, is present to the extent of 2—3 per cent., together with atranoric acid, in *Diploschistes scruposus* (*Patellaria scruposa* or *Urceolaria scruposa*); it crystallises in short needles or rosettes of leaflets melting at 164—165°; its mol. weight was determined in acetone solution; it dissolves in alkali hydroxides to a yellow solution; its alcoholic solution is coloured violet by ferric chloride, and with bleaching powder it gives first a red, then a violet, and finally an indigo coloration. It is converted by acetic acid into orsellic acid, by alcohol into ethyl orsellate; it immediately reduces potassium permanganate, and is changed by potassium hydroxide into a substance resembling orcinol. From these characters it is concluded that this acid is a derivative of orsellic acid, but different from patellic acid and other orsellic acid derivatives. It is suggested that the acid described by Hesse as lecanoric acid in *Urceolaria bryophila* is impure diploschistessic acid. *Cladina rangiferina* contains, together with atranoric acid, fumarprotocetraric acid and not cetraric acid. In *Cladina destricta* the presence of destrictic acid cannot be affirmed, although a colourless compound is present together with *l*-usnic acid.

Cladina silvatica (*Cladonia rangiferina* var. *silvatica*) contains *d*-usnic acid ($[\alpha]_D$ + 491·4° in chloroform solution at 22°), and thus differs from other Cladoniaceæ; the cetrarin also present is probably fumarprotocetraric acid.

The lichen, *Cladina silvatica* var. *spumosa* (*Cladonia rangiferina* var. *spumosa* or *Cladonia silvatica* var. *sylvestris*) cannot be regarded, as hitherto, simply as a variety of *Cladina silvatica*, since it contains 0·7 per cent. of *l*-usnic acid ($[\alpha]_D$ − 490·8° at 17° in chloroform solution). It is rather to be regarded as a variety of *Cladina alpestris*, and named *Cl. alpestris* var. *spumosa*.

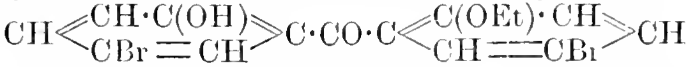
Leiphæmin, which is found in *Hæmatomma leiphaemum*, forms rhombic crystals. In the lichen, *Hæmatomma porphyrium*, $\frac{1}{2}$ per cent. of atranoric acid, 1 per cent. of zeorin, 1 per cent. of porphyrilic acid, 1 per cent. of leiphæmin, and a small amount of hymenorhodin are found. The last mentioned crystallises in rhombic, red plates and gives purple or violet colorations with alkalis and sulphuric acid; it would thus appear to be an anthracene derivative. These facts show that the view that *Hæmatomma porphyrium* and *H. leiphaemum* are identical is untenable. *Hæmatomma coccineum* (*Hæmatomma coccineum* var. *ochroleucum* or *Lecanora hæmatomma coccinea*) contains *l*-usnic acid $2\frac{1}{2}$, zeorin $\frac{1}{2}$, atranoric acid about 1/3, porphyrilic acid 2, and leiphæmin 2 per cent., also a very small quantity of hymenorhodin; Hesse's hæmatommidin is probably identical with leiphæmin.

Parmelia Mougeotti contains *d*-usnic acid.

Lepraria candelaris contains 20—22 per cent. of calycin; the presence of pinastric acid was not established. *Cyphelium trichiale* var. *candelare* contains 8 per cent. of calycin. K. J. P. O.

o-Nitrobenzophenone and its Reduction Products. CARLO BAEZNER and AUGUST GARDIOL (*Ber.*, 1906, 39, 2512—2514).—*Phenyldihydroanthranil*,

$C_6H_4<\genfrac{}{}{0pt}{}{CHPh}{NH—}>O$, is prepared by reduction of o-nitrobenzophenone with aluminium amalgam in ethereal solution, or electrolytically in aqueous-alcoholic sodium acetate solution, with a lead cathode and a lead anode in cold saturated aqueous sodium carbonate; it forms glistening, pale yellow crystals and melts at 116·5°. G. Y.

Observations in the Diphenylmethane and Xanthone Series. OTTO DIELS and KARL ROSENMUND (*Ber.*, 1906, 39, 2358—2364).—The substance formerly described as 5:5′-dibromo-2-hydroxy-2′-ethoxybenzophenone,

$CH\lessgtr\genfrac{}{}{0pt}{}{CH\cdot C(OH)}{CBr=CH}>C\cdot CO\cdot C\lessgtr\genfrac{}{}{0pt}{}{C(OEt)\cdot CH}{CH=CBr}>CH$ (Abstr., 1905, i, 432), is shown by the following facts to have this structure, and not that of an alcoholate of 2:7-dibromoxanthone, as might be supposed from the ease with which it is converted into the latter substance. The reason for its instability is discussed at length.

With phenylhydrazine, the substance gives the *phenylhydrazone*, $OH\cdot C_6H_3Br\cdot C(:N_2HPh)\cdot C_6H_3Br\cdot OEt$, which crystallises from alcohol in yellow needles and melts at 165°. The *oxime*,

$$OH\cdot C_6H_3Br\cdot C(:NOH)\cdot C_6H_3Br\cdot OEt,$$

crystallises from chloroform and melts at 181—182°. The *acetyl* derivative, $OAc\cdot C_6H_3Br\cdot CO\cdot C_6H_3Br\cdot OEt$, is easily obtained by direct acetylation, crystallises from alcohol in needles, and melts at 105—107°.

The monoethyl ether is easily reconverted into the diethyl ether, $CO(C_6H_3Br\cdot OEt)_2$, by treating it with potassium in benzene solution and heating the product with ethyl iodide. The ease, however, with which it is converted into 2 : 7-dibromoxanthone is shown by the fact that this substance begins to separate almost immediately on heating with $N/20$ potassium hydroxide.

5 : 5′-*Dibromo*-2 : 2′-*dimethoxydiphenylmethane*, $CH_2(C_6H_3Br\cdot OMe)_2$, prepared by adding 20 per cent. formaldehyde to a solution of *p*-bromoanisole in dilute sulphuric acid at −10°, crystallises from alcohol and melts at 108°. On oxidation with chromic acid in glacial acetic acid solution, it gives 5 : 5′-*dibromo*-2 : 2′-*dimethoxybenzophenone*,

$$CO(C_6H_3Br\cdot OMe)_2,$$

which crystallises from alcohol or glacial acetic acid and melts at 123°; on heating this with concentrated hydrochloric acid for five hours at 160°, 5 : 5′-*dibromo*-2-*hydroxy*-2′-*methoxybenzophenone*,

$$OH\cdot C_6H_3Br\cdot CO\cdot C_6H_3Br\cdot OMe,$$

is obtained. The latter crystallises from alcohol in deep yellow needles, melts at 159°, and differs from the analogous ethoxy-derivative in giving 5 : 5′-*dibromo*-2 : 2′-*dihydroxybenzophenone*,

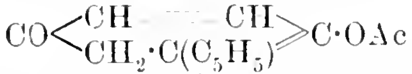
$$CO(C_6H_3Br\cdot OH)_2,$$

when it is heated with aluminium chloride and the product decomposed by water; the dihydroxy-compound crystallises from light petroleum in yellow leaflets, melts at 138·5°, and differs from its monomethyl and monoethyl ethers by not being convertible into dibromoxanthone by concentrated acids or alkalis, or by phosphoric oxide or zinc chloride. With diazomethane, however, yellow needles melting at 156° are obtained, which, on heating with alkali, readily give the 2 : 7-dibromoxanthone. W. A. D.

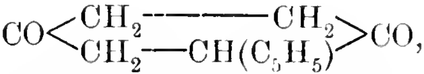
Hydrobenzoin. August Klages (*Ber.*, 1906, **39**, 2356—2357).—The product obtained by treating benzoin according to Apitzsch and Metzger's method (Abstr., 1904, i, 510) is not hydrobenzoin, but unchanged benzoin; its true nature is shown by the properties of its derivatives. Apitzsch and Metzger were probably led into error owing to the melting point of hydrobenzoin being identical with that of benzoin. W. A. D.

Additive Products of *cyclo*Pentadiene and Quinones. Walther Albrecht (*Annalen*, 1906, **348**, 31—49).—With 1—2 mols. of *cyclo*pentadiene, benzoquinone forms *additive* compounds, to which no satisfactory constitutions can be ascribed; those given are in accordance with most of the properties of the substances, but not with the reduction of *cyclo*pentadienequinone to a dihydro-derivative which is not a quinol, nor with the stability of the chloranil derivative of *cyclo*pentadiene.

cyclo*Pentadienebenzoquinone*,  $CH{<}\begin{matrix}CH-CO\\CO\cdot CH_2\end{matrix}{>}CH\cdot C_5H_5$, formed with development of heat by the action of 1 mol. of *cyclo*pentadiene on 1 mol. of benzoquinone in cooled alcoholic solution, crystallises in long, slender, slightly yellow needles, or flat, greenish-yellow prisms, melts at 77—78°, decomposes into its generators when more highly heated, is readily soluble in organic solvents, and gives in alkaline solution a deep red to yellow, in concentrated sulphuric acid a red coloration, and a blue, flocculent precipitate on addition of water. It forms an intense blue solution when heated with zinc chloride and glacial acetic acid, reduces ammoniacal silver nitrate at the ordinary temperature and Fehling's solution on boiling, forms an unstable *dibromide*, and gives precipitates with hydroxylamine and phenylhydrazine. When evaporated with acetic anhydride, *cyclo*pentadienebenzoquinone yields quinol diacetate, but forms a *monoacetyl* derivative,

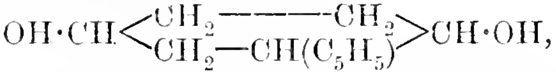

$CO{<}\begin{matrix}CH=\!=\!=CH\\CH_2\cdot C(C_5H_5)\end{matrix}{\geqslant}C\cdot OAc$ or  $OAc\cdot C{\leqslant}\begin{matrix}CH=\!=CH\\CH\cdot CH(C_5H_5)\end{matrix}{>}CO$,

when treated with acetic anhydride and cooled concentrated sulphuric acid; this crystallises in white needles, melts at 91—92°, gives a blue coloration with glacial acetic and concentrated sulphuric acids, and yields benzoquinone when boiled with ferric chloride solution. The *semicarbazone* of *cyclo*pentadienebenzoquinone, $C_{13}H_{16}O_2N_6$ or $C_{13}H_{18}O_3N_6$, forms a fine, white powder, decomposes at about 220°, and gives an intense yellow coloration with concentrated sulphuric acid.

cyclo*Pentadienedihydrobenzoquinone*,  $CO{<}\begin{matrix}CH_2-\!-\!-\!-CH_2\\CH_2-CH(C_5H_5)\end{matrix}{>}CO$, formed by reduction of *cyclo*pentadienebenzoquinone by zinc dust in glacial acetic acid solution, separates from alcohol in white crystals, melts at 34—35°, decomposes when distilled, forming *cyclo*pentadiene and quinol, is soluble in the usual solvents, gives a reddish-violet coloration with concentrated sulphuric acid, reduces ammoniacal silver nitrate and Fehling's solutions at the ordinary temperature, and is converted by concentrated potassium hydroxide into an insoluble, white *polymeride*, $(C_{11}H_{12}O_2)_x$, melting above 270°. The dihydrodiketone forms a yellow *precipitate* with phenylhydrazine in aqueous solution, a *semicarbazone* melting at 222—224°, and with Baeyer's reagent a *ferrocyanide* crystallising in long, colourless needles. The *dioxime*, $C_{11}H_{14}O_2N_2$, crystallises in white needles and decomposes at 188°. With bromine in ethereal solution, the dihydrodiketone forms a *hydroxybromide*, $C_{11}H_{12}O_2Br\cdot OH$, which crystallises in colourless prisms, melts at 132—133°, absorbs 1 mol. of bromine in chloroform solution, and when boiled with a copper-zinc couple and acetic acid in alcoholic solution yields the dihydrodiketone. The *dibromide*, $C_{11}H_{12}O_2Br_2$, is formed in slender needles by the action of hydrogen bromide on the hydroxybromide in chloroform solution and melts at 138—139°. The action of methyl-alcoholic potassium hydroxide on the hydroxybromide leads to the formation of the *oxide*, $C_{11}H_{12}O_3$, which crystallises in small prisms, melts at 149—150°, and re-forms the hydroxybromide when treated with hydrogen bromide in glacial acetic acid solution.

The *pinacone*, $C_{22}H_{22}O_4$, formed together with the dihydrodiketone by the reduction of *cyclo*pentadienebenzoquinone with zinc dust, crystallises in white leaflets, melts at 188—189°, gives a reddish-violet coloration with concentrated sulphuric acid, reduces ammoniacal silver nitrate on boiling, or dilute potassium permanganate at the ordinary temperature, and forms a deep red, sparingly soluble *product* with phenylhydrazine.

trans-cyclo*Pentadienedihydroquinol*,

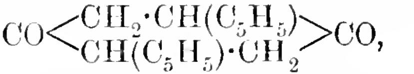


$$OH{\cdot}CH\begin{matrix}\diagup CH_2 \text{———} CH_2 \diagdown \\ \diagdown CH_2\text{—}CH(C_5H_5) \diagup\end{matrix}CH{\cdot}OH,$$

prepared together with a yellow oil, $C_{11}H_{16}O_2,\frac{1}{2}H_2O$, which is probably the cis-*form*, by reduction of dihydro*cyclo*pentadienebenzoquinone with sodium amalgam, crystallises in stellate aggregates of needles, melts at 88°, and on exposure to air absorbs $\frac{1}{2}H_2O$, forming dull crystals melting at 96—98°. The *dibenzoate*, $C_{25}H_{24}O_4$, crystallises in slender needles and melts at 166—167°.

With chloranil, *cyclo*pentadiene reacts in benzene solution in presence of trimethylamine, forming the *additive* compound, $C_{11}H_6O_2Cl_4$, which crystallises from absolute alcohol in long, strongly refracting, yellow needles, melts at 146—146·5°, gives with concentrated sulphuric acid a violet, with alcoholic potassium hydroxide a yellowish-red solution, reduces ammoniacal silver nitrate on boiling, reacts violently with phenylhydrazine, and with bromine in chloroform solution in direct sunlight forms a *dibromide*, $C_{11}H_6O_2Cl_4Br_2$, crystallising in glistening, white leaflets and melting at 269°.

cyclo*Pentadiene-α-naphthaquinone*, $C_{15}H_{12}O_2$, prepared from *cyclo*pentadiene and α-naphthaquinone in benzene solution, crystallises in slender, white prisms, melts at 115—116°, reduces ammoniacal silver and Fehling's solutions at the ordinary temperature, gives a red coloration with alkali hydroxides or concentrated sulphuric acid, and forms *precipitates* with phenylhydrazine and semicarbazide acetates.



*Di*cyclo*pentadienebenzoquinone*, $CO\begin{matrix}\diagup CH_2{\cdot}CH(C_5H_5) \diagdown \\ \diagdown CH(C_5H_5){\cdot}CH_2 \diagup\end{matrix}CO$, formed by the action of 2 mols. of *cyclo*pentadiene on 1 mol. of benzoquinone in benzene or alcoholic solution, crystallises in glistening, white leaflets or needles, melts at 157—158°, is soluble in organic solvents, only slightly volatile in a current of steam, is insoluble in aqueous alkali hydroxides, reduces ammoniacal silver and Fehling's solutions on boiling, behaves in the same manner as *cyclo*pentadienebenzoquinone towards concentrated sulphuric acid and zinc and ferric chlorides, and forms a red *oil* with phenylhydrazine and an insoluble white *disemicarbazone*, melting above 270°. The *dioxime*, $C_{16}H_{18}O_2N_2$, crystallises from alcohol, becomes brown at 185°, and does not melt at 270°. With bromine in chloroform solution, di*cyclo*pentadienebenzoquinone forms a *dibromide* which, on recrystallisation from alcohol, yields the *ethoxybromide*, $C_{18}H_{21}O_3Br$, crystallising in slender, white needles and melting at 142°. The *methoxybromide*, $C_{17}H_{19}O_3Br$, crystallises in slender, white needles and melts at 188°.

*cyclo*Pentadiene does not react with anthraquinone, phenanthraquinone, β-naphthaquinone, benzil, benzylideneacetone, phorone, or dibenzoylstyrene. G. Y.

Anthraquinone-α-sulphonic Acids. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 167169).—α-Nitroalizarin and α-nitroanthraquinonesulphonic acids behave like α-nitroanthraquinone on treatment with hot aqueous alkali sulphites, the α-nitro-group being replaced by a sulpho-group.

α-Nitroalizarin and α-nitroanthraquinone-6-sulphonic acid, when treated in this way, give rise to alizarin-α-sulphonic and anthraquinone-1 : 6-disulphonic acids respectively. The α-nitroanthraquinonesulphonic acids, containing their sulphonic groups in positions 5, 7, and 8, behave in a similar manner. G. T. M.

Preparation of Anthraquinone-di- and -tri-sulphonic Acids. R. WEDEKIND & CO. (D.R.-P. 170329).—Potassium anthraquinone-α-sulphonate, when sulphonated with fuming sulphuric acid in the presence of mercury, yields anthraquinone-1 : 5- and -1 : 8-disulphonic acids. In the absence of mercury, the sulphonation leads to the production of the 1 : 7- and 1 : 6-disulphonic acids and a trisulphonic acid of unknown constitution. On heating this mixture of acids under pressure with milk of lime containing calcium chloride and potassium nitrate, 1 : 7- and 1 : 6-dihydroxyanthraquinones are produced, together with about 25 per cent. of a new *dihydroxyanthraquinonesulphonic acid*, the *barium* salt, $C_{28}H_{14}O_{14}S_2Ba$, of which crystallises from hot water in orange needles. G. T. M.

Preparation of the Carbamates of the Nitroaminoanthraquinones. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 167410).—*o*-Nitro-derivatives of the aminoanthraquinones cannot be prepared either from the aminoanthraquinones themselves or from their acyl derivatives. In the former case, the nitration does not proceed smoothly, and in the latter only *p*-nitro-derivatives are produced. Nitration of the carbamates of the aminoanthraquinones, however, leads to the production of the important *o*-nitroamino-derivatives. The *carbamate* of β-aminoanthraquinone, obtained by heating together β-aminoanthraquinone and ethyl chlorocarbonate in nitrobenzene solution, separates on cooling in golden-yellow leaflets; on nitration with a mixture of concentrated nitric and sulphuric acids, it yields 1-nitro-2-aminoanthraquinone and 3-nitro-2-aminoanthraquinone, these isomerides being separated by crystallisation from nitrobenzene, in which the latter is the less soluble. Similarly, the carbamate of α-aminoanthraquinone furnishes a mixture of the ortho- and para-nitro-compounds, which are also separated by means of nitrobenzene, in which the para-isomeride is the less soluble. G. T. M.

Preparation of α-Nitro-β-methoxyanthraquinones. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 167699).—The energetic nitration of anthraquinone in concentrated sulphuric acid solution gives rise to the 1 : 5- and 1 : 8-dinitroanthraquinones as chief products, but 40 per cent. of the nitrated material consists of a mixture of other isomerides which have been separated by fractional crystallisation from nitrobenzene and other solvents and characterised by conversion into dimethoxyanthraquinones and dihydroxyanthraquinones successively.

The ββ-dinitroanthraquinones are present only in very small quantities in the product of nitration. The αβ-isomerides, of which the 1 : 6-compound is formed in largest amount, behave differently from the αα-compounds towards sodium methoxide. In the αβ-series, the β-nitro-group is readily replaced by methoxyl, and an α-nitro-β-methoxyanthraquinone results; the αα-compounds are attacked only with great difficulty, and then both nitro-groups are replaced by methoxyl.

1-*Nitro-6-methoxyanthraquinone* is readily formed by heating together 1 : 6-dinitroanthraquinone and sodium methoxide in methyl alcohol; it crystallises from benzene in lustrous, yellow leaflets melting at 268°. With concentrated sulphuric acid, the methoxy-derivative develops an orange colour; it dissolves in aqueous sodium sulphide to a pale bluish-green solution, from which, on warming, 1-amino-6-methoxyanthraquinone separates as an orange-yellow precipitate.

1-*Nitro-7-methoxyanthraquinone* crystallises from benzene in slightly coloured needles melting at 238°; on reduction with sodium sulphide, it furnishes the orange-red 1-amino-7-methoxyanthraquinone.

These methoxy-derivatives are readily hydrolysed to α-nitro-β-hydroxyanthraquinones by concentrated hydrochloric and acetic acids. The α-amino-β-hydroxyanthraquinones may be obtained either by reducing the α-nitro-β-hydroxy-derivatives or by hydrolysing the α-amino-β-methoxy-derivatives.

The patent contains a table of the properties of the dinitro- and dimethoxy-anthraquinones. G. T. M.

A New Derivative of Anthraquinone. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 167461).—Although the fusion of erythrohydroxyanthraquinone with potassium hydroxide furnishes a certain amount of alizarin, yet the main product of this reaction is a *substance*, $C_{28}H_{14}O_6$, hitherto uncharacterised, which, in view of its sparing solubility, is probably formed by the condensation of 2 molecules of erythrohydroxyanthraquinone; the alkali salts of this compound, which are also very insoluble, point to its being a hydroxy-derivative. It crystallises from diphenylmethylamine in golden-yellow needles, and yields with alkaline solutions of sodium hyposulphite a leuco-derivative which is somewhat more soluble in aqueous alkali.

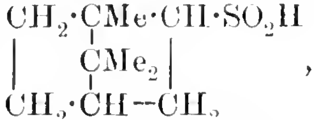
G. T. M.

Preparation of *p*-Mono- and *p*-Di-chloroanthrarufin. R. WEDEKIND & CO. (D.R.-P. 167743).—Hitherto anthrarufin has only been successfully chlorinated when suspended or dissolved in glacial acetic acid. It is now found that when suspended in dilute sulphuric acid boiling at 140° and treated slowly with the calculated amount of potassium chlorate and sodium chloride in aqueous solution, anthrarufin may be quantitatively converted into either *p*-mono- or *p*-chloroanthrarufin. G. T. M.

[Sulphonation of α-Hydroxyquinizarin-green.] FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 170113).—α-Hydroxyquinizarin-green, $HO\cdot C_6H_3<{CO \atop CO}>C_6H_2(NH\cdot C_7H_7)_2$, when sulphonated in the usual way, yields mono- and di-sulphonic derivatives containing the sulpho-groups in the toluene nuclei. When, however, the sulphonation is effected by fuming sulphuric acid in the presence of boric acid, the sulpho-groups enter the anthraquinone residue exclusively. The sodium salt of the resulting sulphonic acid,

$$NaSO_3\cdot C_6H_2(OH)<{CO \atop CO}>C_6H_2(NH\cdot C_7H_7)_2,$$

is sparingly soluble in hot water, but dissolves more readily in dilute acetic acid. Its colour in concentrated sulphuric acid is violet-blue, whereas the other sulphonic acids of α-hydroxyquinizarin-green develop greenish-blue or bluish-green colorations. G. T. M.

Thioborneol and other Derivatives of Camphane containing Sulphur. WALTHER BORSCHE and W. LANGE (*Ber.*, 1906, **39**, 2346—2356).—*Camphane-2-sulphinic acid*, 
$$\begin{array}{l} CH_2\cdot CMe\cdot CH\cdot SO_2H \\ | \qquad CMe_2 \qquad | \\ CH_2\cdot CH-CH_2 \end{array}$$
, prepared by saturating an ice-cold ethereal solution of magnesium camphyl chloride with sulphur dioxide, forms a colourless syrup, which is only sparingly soluble in water; when cooled in a mixture of ice and salt, it gelatinises, but does not crystallise. The *sodium* salt, $C_{10}H_{17}\cdot SO_2Na$, crystallises from water.

Methylcamphylsulphone, $C_{10}H_{17}\cdot SO_2Me$, prepared by warming the sulphinic acid with alcoholic sodium ethoxide and methyl iodide, crystallises from dilute alcohol in long, slender needles and melts at 57—58°. 1 : 4-*Dihydroxyphenyl-2-camphylsulphone*,

$$C_{10}H_{17}\cdot SO_2\cdot C_6H_3(OH)_2,$$

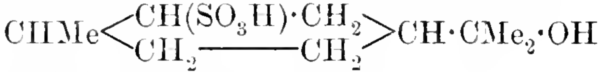
prepared by the action of the sulphinic acid on benzoquinone, separates from benzene or glacial acetic acid in colourless crystals and melts at 186—187°.

Camphane-2-sulphonic bromide, $C_{10}H_{17}\cdot SO_2Br$, prepared by the action of bromine at 0° on camphylsulphinic acid dissolved in aqueous potassium hydroxide, forms a nearly colourless oil, which, with ammonia, gives *camphane-2-sulphonamide*; this crystallises from a mixture of benzene and light petroleum and melts at 122—123°.

Thioborneol (*camphyl hydrosulphide*), $C_{10}H_{17}\cdot SH$, prepared either by reducing camphane-2-sulphonic bromide with tin and hydrochloric acid or by adding powdered sulphur to an ethereal solution of magnesium camphyl chloride, boils at 205—215° and separates from dilute alcohol as a white, crystalline mass which soon becomes caked to a glassy product; it softens gradually when heated, without melting at any definite temperature; at 50°, it is completely liquid. By air it is oxidised to *camphyl disulphide*, $(C_{10}H_{17})_2S_2$, which separates from dilute alcohol in flocculent masses of crystals and melts (when not fully purified) at 121°. The *mercuric chloride* derivative, $C_{10}H_{17}\cdot S\cdot HgCl$, of thioborneol is a white powder; the *lead* derivative, $(C_{10}H_{17}S)_2Pb$, forms lustrous, yellow crystals.

Methyl camphyl sulphide (*thioborneol methyl ether*), $C_{10}H_{17}\cdot SMe$, is best prepared by warming methyl iodide with an ethereal solution of the crude product of the action of sulphur on magnesium camphyl chloride; it forms a yellow oil, which boils at 110—115°, and combines with methyl iodide, giving *dimethylcamphylsulphonium iodide*, $C_{12}H_{23}SI$; this crystallises from water, undergoing but slight decomposition in the process, in colourless plates, melts at 148—148·5°, and is converted by moist silver oxide into *dimethylcamphylsulphonium hydroxide.* The latter forms hygroscopic leaflets, melts at 140—141°, and gives a crystalline *platinichloride*, $(C_{12}H_{23}S)_2PtCl_6$, which melts at 142—143°.

Camphane-2-sulphinic acid, on oxidation with potassium permanganate, gives not the corresponding sulphonic acid, but the *sulphonic acid* of a *camphane hydrate*, which is, perhaps, either

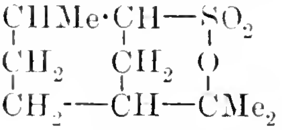


$$CHMe<\begin{matrix}CH(SO_3H)\cdot CH_2\\ CH_2\text{———}CH_2\end{matrix}>CH\cdot CMe_2\cdot OH$$

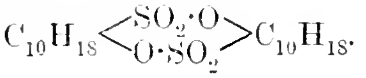
or

$$OH\cdot CMe<\begin{matrix}CH(SO_3H)\cdot CH_2\\ CH_2\text{———}CH_2\end{matrix}>CHMe_2.$$

The same substance is obtained on hydrolysing camphane-2-sulphonic bromide with 10 per cent. aqueous potassium hydroxide. The *potassium* salt, $C_{10}H_{19}O_4SK$, crystallises from absolute alcohol and gives, with phosphorus pentachloride, *camphane hydrate sulphonic chloride*, $C_{10}H_{19}\cdot SO_2Cl$, which forms colourless crystals and melts at about 95°. On reducing this sulphonic chloride with tin and hydrochloric acid, a *product* having the composition $C_{10}H_{18}O_3S$ is obtained, which separates from methyl or ethyl alcohol in colourless crystals and is reconverted into potassium camphane hydrate sulphonate by heating with dilute aqueous potassium hydroxide. The substance $C_{10}H_{18}O_3S$ is perhaps the *auto-ester*,



or



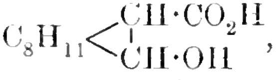
$$C_{10}H_{18}<\begin{matrix}SO_2\cdot O\\ O\cdot SO_2\end{matrix}>C_{10}H_{18}.$$

W. A. D.

Constitution of Camphor and its Derivatives. IX. Electrolytic Reduction of Camphorcarboxylic Acid to Borneolcarboxylic Acid and Dehydroborneolcarboxylic Acid.

JULIUS BREDT [and KARL BURKHEISER] (*Annalen*, 1906, **348**, 199—209).—When reduced electrolytically in potassium carbonate solution with a cathode of potassium amalgam, an *E.M.F.* of 30 volts, and a current of 7—7·5 amperes, the temperature remaining below 30°, camphorcarboxylic acid yields borneolcarboxylic acid and an *isomeride* which crystallises in needles and melts at 101—102°.

Borneolcarboxylic acid (*β-hydroxycamphanecarboxylic acid*),



$$C_8H_{11}<\begin{matrix}CH\cdot CO_2H\\ |\\ CH\cdot OH\end{matrix},$$

crystallises from boiling water in silky needles, melts at 170—171°, and when quickly heated distils at 190° under 13 mm. pressure. The *calcium* salt, $(C_{11}H_{17}O_3)_2Ca$, was analysed. When repeatedly distilled slowly under 13 mm. pressure into a sealed receiver, the acid loses water and yields *dehydroborneolcarboxylic acid* (*camphenecarboxylic acid*), $C_{11}H_{16}O_2$, which crystallises in fan-like aggregates of long needles, melts at 112—113°, is volatile in a current of steam, and decolorises potassium permanganate, being oxidised to a crystalline *acid* melting at 209—210°.

Borneolcarboxylic acid is probably related to *trans*-camphylglycol (Farbwerke vorm. Meister, Lucius, & Brüning, Abstr., 1902, i, 299) as a hydroxy-acid to its glycol, dehydroborneolcarboxylic acid corresponding with dehydrocamphylcarbinol. G. Y.

Carvone. HANS RUPE (*Ber.*, 1906, 39, 2372. Compare Rupe and Dorschky, this vol., i, 595).—Carvone semicarbazone, melting at 162°, has $[\alpha]_D$ +115·1° at 20°; the semicarbazone melting at 141—142° has $[\alpha]_D$ +113·3° at 20°. W. A. D.

Action of Sodamide on Cyclic Ketones. Derivatives of Fenchone and of Camphenilone, and their Constitution. FRIEDRICH W. SEMMLER (*Ber.*, 1906, 39, 2577—2582).—*Dihydrofencholenamide* (*b*), $C_{10}H_{19}ON$, is obtained in quantitative yield when sodamide (1 mol.) and fenchone (1 mol.) react for four hours in boiling benzene; it melts at 94°, boils at 160° under 11 mm. pressure, and with concentrated sulphuric acid and potassium nitrite gives a brown coloration changing through red to green. A 25 per cent. ethereal solution has α_D about +1° in a 100 mm. tube. The substance is different from Mahla's amide (Abstr., 1902, i, 106), which is subsequently called dihydrofencholenamide (*a*).

By hydrolysis with alcoholic potash, *dihydrofencholenic acid* (*b*), $C_{10}H_{18}O_2$, is obtained; it solidifies at the ordinary temperature, boils at 140—141° under 10 mm. pressure, has a sp. gr. 0·9742 at 15°, n_D 1·45862, and α_D +3°12′ in a 100 mm. tube. The *methyl* ester, $C_{11}H_{20}O_2$, boils at 91° under 12 mm. pressure, has a sp. gr. 0·9295 at 22°, n_D 1·44260, and α_D +3·0° in a 100 mm. tube. The *ethyl* ester boils at 97° under 10 mm. pressure, has a sp. gr. 0·9129 at 20°, n_D 1·43958, and α_D +3·5° in a 100 mm. tube. Dihydrofencholenic acid (*a*) boils at 140·5—141° under 10 mm. pressure, has a sp. gr. 0·9742 at 20°, n_D 1·45962, and α_D +4·10° in a 100 mm. tube (compare Mahla, *loc. cit.*); the *methyl* ester boils at 90° under 9 mm. pressure, has a sp. gr. 0·93306 at 22°, n_D 1·44662, and α_D +3° in a 100 mm. tube. *Dihydrofencholenyl alcohol* (*b*), $C_{10}H_{20}O$, obtained in an 80 per cent. yield by reducing the ethyl ester of the acid with sodium and alcohol, boils at 100° under 11 mm. pressure, has a sp. gr. 0·8869 at 22°, n_D 1·45662, and α_D +10° in a 100 mm. tube; the *acetate*, $C_{10}H_{19}OAc$, boils at 112—113° under 14 mm. pressure, has a sp. gr. 0·9123 at 22°, n_D 1·44159, and α_D +12·44° in a 100 mm. tube; the *phthalate*,

$$CO_2H{\cdot}C_6H_4{\cdot}CO_2{\cdot}C_{10}H_{19},$$

melts at 86°, the *silver* salt at 113°.

The corresponding (*a*) alcohol boils at 99—100° under 10 mm. pressure, has a sp. gr. 0·9072 at 22°, and n_D 1·45762. *Dihydrofencholenaldehyde* (*b*), $C_{10}H_{18}O$, boils at 80—85° under 10 mm. pressure, has a sp. gr. 0·885 at 20°, and n_D 1·445; the *semicarbazone* melts at 144—145°.

When camphenilone is treated with sodamide in benzene solution, *dihydrocamphoceenamide* (*b*), $C_9H_{17}ON$, is obtained; it melts at 168°, and by hydrolysis with alcoholic potash yields the *acid* (*b*), $C_9H_{16}O_2$, which boils at 138—139° under 12 mm. pressure, has a sp. gr. 0·9815 at 22°, and n_D 1·45662. C. S.

Synthesis of $\Delta^{8(9)}$-Menthene and of Active $\Delta^{3.8(9)}$-Menthadiene.

Friedrich W. Semmler and Ch. Rimpel (*Ber.*, 1906, **39**, 2582—2587).—iso*Pulegyl chloride*, $C_{10}H_{17}Cl$, is obtained quantitatively when *iso*pulegole (1 mol.) dissolved in light petroleum is slowly added to phosphorus pentachloride (1 mol.) in the same solvent, rise of temperature being avoided; it boils at 85—90° under 12 mm. pressure, has a sp. gr. 0·9600 at 20°, n_D 1·47740, a_D +19·15° (100 mm. tube), and by treatment with alcoholic potash yields iso*pulegyl ethyl ether*, $C_{10}H_{17}\cdot OEt$, which boils at 85—88° under 14 mm. pressure and has a sp. gr. 0·8972 at 20°.

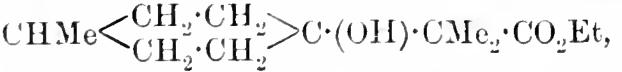
$\Delta^{8(9)}$-*Menthene*, $C_{10}H_{18}$, is obtained when *iso*pulegyl chloride is treated with sodium and boiling alcohol. It boils at 53—55° under 14 mm. pressure, has a sp. gr. 0·8104 at 20°, n_D 1·45662, and is optically inactive. By oxidation with dilute permanganate, it yields p-*menthane*-8 : 9-*diol*, $C_{10}H_{18}(OH)_2$, which boils at 165° under 26 mm. pressure, and is oxidised by chromic acid to p-*methylhexahydroacetophenone*, $C_9H_{16}O$, which boils at 70—73° under 13 mm. pressure, has a sp. gr. 0·8982 at 20°, n_D 1·44561, is optically inactive, forms a *semicarbazone*, $C_{10}H_{19}ON_3$, melting at 164—165°, and is oxidised by bromine in alkaline solution to *p*-hexahydrotoluic acid, $C_8H_{14}O_2$, which melts at 108°.

$\Delta^{3.8(9)}$-*Menthadiene*, $C_{10}H_{16}$, is the chief product obtained when *iso*pulegyl chloride dissolved in quinoline is added to quinoline at 200—210°; it boils at 62—65° under 14 mm., or at 174—177° under the ordinary pressure, has a sp. gr. 0·8420 at 20°, n_D 1·48422, and a_D +15° (100 mm. tube). The presence of a conjugated system of two double linkings is proved by the fact that the hydrocarbon absorbs only two atoms of bromine.

The physical properties of Perkin's compounds (Trans., 1905, **87**, 639; 1906, **89**, 839) do not agree with the preceding data; the discrepancy is attributed to intramolecular change, which occurs in the synthesis of Perkin's $\Delta^{8(9)}$-menthene and $\Delta^{3.8(9)}$-menthadiene. C. S.

Synthesis of Menthene.

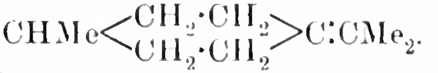
Otto Wallach (*Ber.*, 1906, **39**, 2504—2505. Compare Semmler, preceding abstract; Perkin, Trans., 1906, **89**, 837).—*Ethyl* 1-*hydroxy*-4-*methyl*cyclo*hexane*-1-iso*butyrate*,



$$\mathrm{CHMe}{<}\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}{>}\mathrm{C\cdot(OH)\cdot CMe_2\cdot CO_2Et}$$

, formed by condensation of 1-methyl*cyclo*hexane-4-one with ethyl *a*-bromo*iso*butyrate in presence of zinc, boils at 148—150° under 16 mm. pressure, and on elimination of water yields *ethyl* 4-*methyl*-Δ^1-cyclo*hexene*-1-iso*butyrate*,

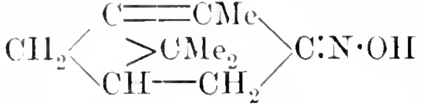
$$CHMe<\begin{matrix}CH_2-CH\\CH_2\cdot CH_2\end{matrix}\gtrless C\cdot CMe_2\cdot CO_2Et,$$

which boils at 123—126° under 13 mm. pressure. The crystalline *acid*, $C_{11}H_{18}O_2$, obtained on hydrolysis of the unsaturated ester, melts at 95—96°, and when distilled slowly loses carbon dioxide and forms i-$\Delta^{4(8)}$-*menthene*,  $CHMe<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>C:CMe_2$. This boils at 172—174°, has a sp. gr. 0·831 and n_D 1·4647 at 21°, and when oxidised with permanganate yields 1-methyl*cyclo*hexane-4-one and acetone. The action of amyl nitrite and hydrochloric acid, or successively of hydrochloric and nitrous acids, on *i*-$\Delta^{4(8)}$-menthene leads to the formation of an *additive* compound, which is obtained as a blue oil, gradually solidifying to white crystals melting at 101—103°. Both forms of the substance are volatile in a current of steam and yield a menthylamine when reduced. When boiled with dilute sulphuric acid, *i*-$\Delta^{4(8)}$-menthene is converted slowly into *i*-Δ^3-menthene. G. Y.

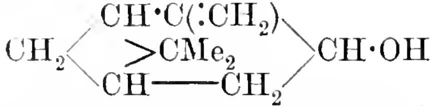
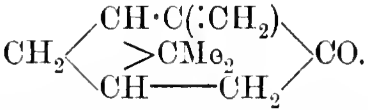
Terpenes and Ethereal Oils. LXXVIII. Pinene Series. OTTO WALLACH (*Annalen*, 1906, **346**, 220—247. Compare Abstr., 1894, i, 45; 1898, i, 485; this vol., i, 370).—The nitrosopinene obtained by the action of alkalis on pinene nitrosochloride is the oxime of an unknown ketone. Attempts have now been made to ascertain which is the ketone corresponding with this oxime, and secondly to determine the chemical relations of pinocarvone, which is obtained from nitrosopinene by conversion into pinylamine and thence into a ketone.

[With FRIEDRICH JÄGER.]—Pinocarveol is prepared by treating a solution of pinylamine with acetic acid and sodium nitrite, warming, and distilling the alcohol in steam; it has still to be separated from small quantities of nitrite and unchanged pinylamine; it is a colourless oil, boiling at 100—102° under 12 mm. pressure, and has a sp. gr. 0·980 and n_D 1·4988 at 18°. The value of the molecular refraction shows that under this treatment the ring in pinylamine is not broken. With phenylcarbimide, pinocarveol yields mainly a well-crystallised product, melting at 82—84°, together with a small amount of a compound melting at 95°. When heated with a hydrogen sulphate or with sulphuric acid or with a solution of sulphuric acid in acetic acid, cymene is obtained in small quantity from pinocarveol. On oxidation with dilute permanganate, small amounts of a *glycol* and an *acid*, $C_9H_{14}O_4$, are formed. Pinocarvone is prepared from the alcohol in the manner previously described (Abstr., 1894, i, 45), and purified by conversion into the semicarbazone, which melts at 204°. The ketone boils at 95° under 12 mm. pressure, has a sp. gr. 0·984, and n_D 1·5050 at 20°; from the value of the molecular refraction it is concluded that pinocarvone is the enolic form of a ketone with one ethylene linking. Pinocarvoneoxime (m. p. 98°) yields on reduction with sodium and alcohol a *base* isomeric with but different from pinylamine; it boils at 87—88° under 12 mm. pressure, and gives a *carbamide* which crystallises in needles melting at 99—100°. When oxidised with potassium permanganate, oxalic acid and a dibasic acid, $C_9H_{14}O_4$, are produced;

the latter melts at 96—97° and boils at 170—180° under 12 mm. pressure. This acid is also formed by oxidation of pinocarveol, and appears to be identical with pinic acid. On this assumption, and using Wagner's formula for pinene, nitrosopinene and pinylamine are respectively represented by the expressions

 and 

Since the reduction of pinocarvoxime yields not pinylamine but an isomeride, it follows that in the replacement of the amino-group by hydroxyl a change in the linking must have taken place. Hence the following formulæ are suggested for pinocarveol and pinocarvone respectively:

 and 

The formation of pinic acid and of cymene is then easily accounted for, but it is not obvious why the piceane ring of pinocarvone does not open with formation of carvone.

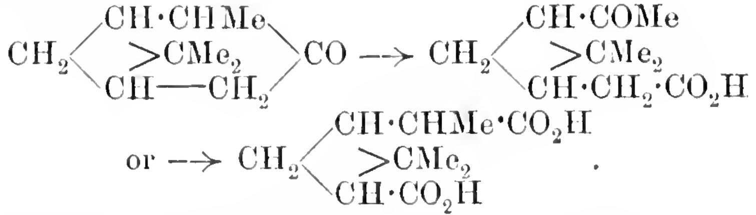
An optically active pinocarveol is contained in the less volatile fraction of the oil of *Eucalyptus globulus*, and is isolated by conversion into the hydrogen phthalate; it boils at 92° under 12 mm. pressure, has a sp. gr. 0·9745 and n_D 1·49630 at 20°, and $[\alpha]_D$ $-52·45°$ in 12·75 per cent. ethereal solution. With phenylcarbimide it yields the same mixture of two compounds as does the artificial product. When oxidised with chromic acid in acetic acid solution, it is converted into a ketone, $C_{10}H_{14}O$, which yields with semicarbazide two *semicarbazones*, a soluble substance melting at 209—210°, and an insoluble, which crystallises in needles melting and decomposing at 320°. The oxime is crystalline and boils at 140° under 20 mm. pressure.

[With Curt Engelbrecht.]—Carvopinone is the ketone corresponding with nitrosopinene, and is obtained when the latter is digested with oxalic instead of mineral acids. It boils at 94—96° under 12 mm. pressure, and yields a characteristic *semicarbazone*, which crystallises in prisms unchanged at 300°. The ketone cannot be re-formed from the semicarbazone in a pure state. With hydroxylamine, nitrosopinene is re-formed. When reduced with sodium and alcohol, an alcohol is produced which on oxidation with chromic acid is converted into pinocamphone.

If a solution of nitrosopinene in acetic acid is boiled with oxalic acid or with 1 mol. of hydrochloric acid, it is directly converted into carvone.

Pinocamphone has been reinvestigated in order to determine whether all its reactions are in accord with the constitution at present assigned to it. With bromine, it readily yields a *dibromide*, $C_{10}H_{14}OBr_2$, which is crystalline and melts at 118—119°.

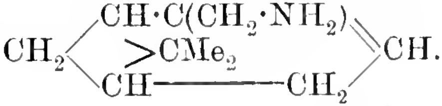
When oxidised by 1 per cent. permanganate or chromic acid in acetic acid solution, a *ketonic acid*, $C_{10}H_{16}O_3$, together with a *dibasic acid*, $C_{10}H_{16}O_4$, are produced; the ketonic acid is separated from the dibasic acid by taking advantage of its solubility in benzene, and is shown by conversion into its semicarbazone to be identical with *a*-pinonic acid. The dicarboxylic acid melts at 186—187°, and is an isomeride of camphoric acid, since by acetyl chloride it is converted into an anhydride. The course of the oxidation is shown by the following scheme:



Pinylamine can be very simply prepared by reducing nitrosopinene with zinc and acetic acid, and, after making alkaline, distilling the base in steam. It boils at 90° under 12 mm. pressure, and has a sp. gr. 0·944 and n_D 1·5062 at 15°, and a sp. gr. 0·94 and n_D 1·5036 at 20°. The value of the molecular refraction indicates the presence of one ethylene linking.

When oxidised with a one per cent. solution of permanganate, pinylamine does not yield pinocarveol, but carvopinone and a *monobasic acid*, $C_9H_{14}O_3$ (?), which forms crystals melting at 89° and boils at 160—170° under 12 mm. pressure; it is not a ketonic acid, neither is it readily oxidised further by chromic acid. The absence of pinocarveol from the oxidation products of pinylamine affords further evidence for the view that, in the change of pinylamine into pinocarveol, a displacement of the linking takes place.

[With Eduard Isaac.]—Further attempts have been made in order to determine whether the nitro-compound obtained from pinene is a true pinene derivative. On reduction with zinc dust and acetic acid, a *base*, $C_{10}H_{17}N$, is obtained, identical with Pesci's aminoterebenthene; it boils at 95° under 12 mm. pressure, and has a sp. gr. 0·9325 and n_D 1·496 at 19° for the base prepared from *d*-pinene, whilst the base obtained from *l*-pinene has a sp. gr. 0·932 and n_D 1·4957 at 20°. Both specimens of the base are lævorotatory. Methylation of the base gives the compound $C_{10}H_{15}NMe_3I$, which melts at 198°.

When the oxalate of the base is treated with nitrous acid and the alcohol thus formed oxidised with chromic acid, a compound with an odour of cuminaldehyde is produced; it yields a semicarbazone melting at 201—203°, and is oxidised by chromic acid to cumic acid (m. p. 115°). From these facts it is deduced that the base aminoterebenthene has the amino-group in the side-chain, probably having the constitution represented by the formula 

K. J. P. O.

Essential Oil of Rue. Henri Carette (*J. Pharm. Chim.*, 1906, [vi], **24**, 58—62. Compare Power and Lees, Trans., 1902, **81**, 1585).—The "summer oil of rue" from Algeria, prepared from *Ruta montana*, is very similar to the oil of rue prepared from *Ruta graveolens*, solidifying at 5—8° and consisting principally of methyl nonyl ketone. Algerian "winter oil of rue," however, is obtained from *Ruta bracteosa*, solidifies at − 15° to − 18°, and consists almost entirely of methyl heptyl ketone; Corsican "oil of rue" is similar, being also obtained from *Ruta bracteosa*. W. A. D.

Correction. OSSIAN ASCHAN (*Ber.*, 1906, **39**, 2596).—In a previous paper on the terpenes of Finnish pines and firs (this vol., i, 442), *Pinus sylvestris* and *P. abies* were incorrectly referred to as the Finland pine and the Finland fir respectively; it should have been the reverse. C. S.

Swedish Turpentine Oil. IWAN L. KONDAKOFF and IWAN SCHINDELMEISER (*Chem. Zeit.*, 1906, **30**, 722—723).—From a sample of Swedish turpentine oil, the authors have isolated *p*-cymene and a small quantity of a hydrocarbon boiling at 145°, which they imagine to be either styrene or toluene. P. H.

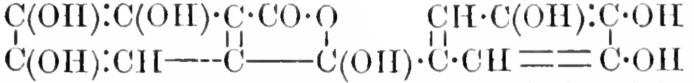
Elemi Resins. V. ALBERT VESTERBERG (*Ber.*, 1906, **39**, 2467—2472. Compare Abstr., 1887, 733; 1891, 165; 1892, 289, 290).—From Manilla elemi, Baup isolated (*Jahresb. Chem.*, 1851, 528), in addition to amyrin, three other crystalline substances, brein, breidin, and bryoidin. The author has separated into two substances, by crystallisation from benzene, the residue in the alcoholic mother liquor from which amyrin has been crystallised. Of these two substances, the one forms colourless, transparent tablets, melts at 216—217°, and appears to be Baup's brein; the other forms thick, yellow prisms and melts at 170—180°. Both, however, give the same *acetate*, $C_{30}H_{48}(OAc)_2$, which melts at 196°, evolves hydrogen bromide on treatment with bromine, and does not give an iodine number.

Brein, $C_{30}H_{48}(OH)_2$ (?), separates from benzene in deliquescent leaflets containing $2C_6H_6$, and from alcohol in small prisms, has $[\alpha]_D$ 65·5° at 15·5° in alcoholic solution, gives a clear yellow liquid with Liebermann's cholesterol reagent, is not affected by sodium and amyl alcohol, and is probably closely related to amyrin, although it is not identical with oxyamyrin. C. S.

Colouring Matter in Saffron. F. DECKER (*Chem. Zeit.*, 1906, **30**, 705).—The potassium or sodium salts of crocetin are obtained by adding alcoholic potassium or sodium hydroxide to a solution of crocetin in dilute aqueous potassium or sodium hydroxide until no further precipitate is formed; on warming the respective solutions, the precipitates dissolve, and are deposited on cooling in crystalline form, the potassium salt in nodular aggregates and the sodium salt in needles.
P. H.

Constitution of Tannin. J. DEKKER (*Ber.*, 1906, **39**, 2497—2502).—A specimen of commercial tannin had $[\alpha]_D + 65°$; when boiled with dilute sulphuric acid, in one hour 51·3 per cent., in two hours 73·4 per cent., and in six hours 74 per cent. of the tannin was converted into gallic acid, the resulting solutions having $[\alpha]_D + 22°$, $+7°$, and $+6°$ respectively.

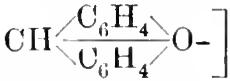
The author considers that tannin must be represented as a derivative of phthalic anhydride,


;

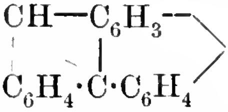
this constitution is in accordance with the optical activity, the almost complete hydrolysis to gallic acid, the formation of diphenylmethane on distillation with zinc dust (Nierenstein, Abstr., 1905, i, 914), the formation of a hexamethyl derivative (Herzig and Tscherne, Abstr., 1905, i, 354), and the absence of a carboxyl group as shown by Boettinger (Abstr., 1884, 318) and by Walden (Abstr., 1899, i, 212).

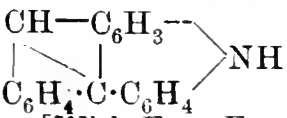
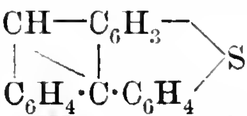
Hexa-acetyltannin is formed, together with triacetylgallic acid, by boiling tannin with acetic anhydride and sodium acetate; it melts at 129° and has $[\alpha]_D + 64·4°$. G. Y.

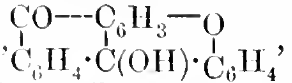
Valency of the Oxygen Atom in Xanthyl Compounds. Double Salts of Xanthyl and Metallic Haloids.

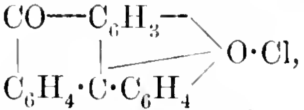
Robert Fosse and L. Lesage (*Compt. rend.*, 1906, **142**, 1543—1545. Compare Abstr., 1905, i, 541, 917).—The author has prepared the following double salts of xanthyl (xanthonium) and metallic haloids: *xanthyl platinichloride*, $PtCl_4,2RCl$ [where R represents ], an orange powder; *xanthyl platinibromide*, $PtBr_4,2RBr$, an orange-yellow precipitate; *xanthyl aurichloride*, $AuCl_3,RCl$, microscopic, yellow crystals; *xanthyl auribromide*, $AuBr_3,RBr$, small, brick-red crystals; *xanthyl uranylchloride*, $UO_2Cl_2,2RCl$, golden-yellow, prismatic crystals; *xanthyl uranyl bromide*, $UO_2Br_2,2RBr$, yellow crystals; *xanthyl ferribromide*, $FeBr_3,RBr$, bright red, microscopic crystals; *xanthyl zincobromide*, $ZnBr_2,2RBr$, orange-yellow crystals; *xanthyl copper bromide*, $CuBr_2,2RBr$, small, dull violet crystals; *xanthyl cadmium bromide*, $CdBr_2,2RBr$, small, yellow crystals; *xanthyl lead bromide*, $2PbBr_2,RBr$, small, clear brown crystals; *xanthyl mercuribromide*, $3HgBr_2,4RBr$, golden-yellow crystals. M. A. W.

Coeroxene, its Derivatives and Isologues.

Herman Decker (*Annalen*, 1906, **348**, 210—250. Compare Baeyer, *Ber.*, 1871, **4**, 555, 658; Orndorff and Brewer, Abstr., 1900, i, 447; 1901, i, 724; Laube, this vol., i, 598).—The name coeroxene is proposed for the parent substance, , of coerulein and coerulin, which become trihydroxycoeroxonone and tetrahydroxycoeroxenol respectively, and the names coeramidine and coerthiene for the isologous cyclic systems,

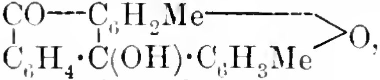
 and , respectively.

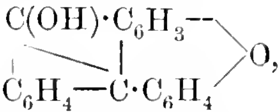
[With Enos Ferrario.]—When treated with ammonia under cooling with ice, *coeroxonium sulphate*, which is prepared by the action of sulphur trioxide on fluoran dissolved in concentrated sulphuric acid below 40°, yields *coeroxonol*,  $\begin{array}{l}CO\text{---}C_6H_3\text{---}O\\ C_6H_4\cdot C(OH)\cdot C_6H_4\end{array}$, which is the carbinol base of the coeroxonium salts. This separates from benzene, ether, chloroform, acetic acid, or acetone in colourless, strongly refracting prisms, becomes violet when heated with a solvent, darkens at 140—160°, and when quickly heated melts and decomposes at 179—180°; it dissolves in dilute mineral acids to form the blood-red oxonium salts, but is almost colourless in acetic acid solution; with dilute hydrochloric acid, an equilibrium is set up between the colourless carbinol, the acid, and the red oxonium salt. When boiled with absolute alcohol, the carbinol forms the *ethyl* ether, $C_{22}H_{16}O_3$, which separates in small, violet, shimmering crystals, melts at 145—146°, and is converted by acids into the oxonium salts. The *oxonium chloride*,



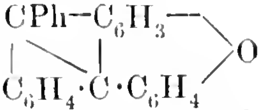
$$\begin{array}{l}CO\text{---}C_6H_3\text{--}\\ \qquad\qquad\qquad\quad > O\cdot Cl,\\ C_6H_4\cdot C\cdot C_6H_4\end{array}$$

crystallises in red needles melting at 185°; the *ferrichloride*, $C_{20}H_{11}O_2FeCl_4$, melts at 233°; the *mercurichloride* melts and decomposes at 228°; the *platinichloride*, $(C_{20}H_{11}O_2)_2PtCl_6$, commences to decompose at 315°; the *bromide*, $C_{20}H_{11}O_2Br$, forms red needles and melts at about 115°; the *tribromide*, $C_{20}H_{11}O_2Br_3$, forms a scarlet precipitate and loses bromine in a desiccator; the *iodide*, $C_{20}H_{11}O_2I$, melts at 216° and is very sparingly soluble; the *picrate, chromate,* and *nitrate* also were prepared.

3 : 13-*Dimethylcoeroxonium sulphate* is formed by the action of sulphur trioxide on dimethylfluoran in sulphuric acid solution; the *carbinol base*,  $\begin{array}{l}CO\text{---}C_6H_2Me\text{------}\\ \qquad\qquad\qquad\qquad\quad > O\\ C_6H_4\cdot C(OH)\cdot C_6H_3Me\end{array}$, melts at 152°; the *ferrichloride*, $C_{22}H_{15}O_2FeCl_4$, melts at 160°.

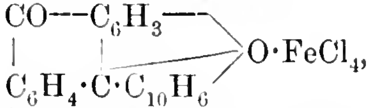
Coeroxenol,  $\begin{array}{l}C(OH)\cdot C_6H_3\text{--}\\ \qquad\qquad\qquad > O\\ C_6H_4\text{---}C\cdot C_6H_4\end{array}$, is prepared by the reduction of coeroxonol in alcoholic alkaline solution, or of coeroxonium salts in acid solution by means of zinc dust, stannous chloride, or hydriodic acid, or by heating phenylxanthenecarboxylic acid with concentrated sulphuric acid at 100°. It crystallises in yellowish-green plates, melts at 136°, dissolves in aqueous alkali hydroxides forming a red, in acetic acid forming a yellow solution with yellow fluorescence, is readily oxidised by air to coeroxonol or coeroxonium salts, and gives a red coloration and green fluorescence in concentrated sulphuric acid. The *acetyl* derivative, $C_{22}H_{14}O_3$, formed by reduction of coeroxonol in a solution containing acetic anhydride, crystallises in dark yellow leaflets, melts at 212°, is not oxidised by air, and is hydrolysed only slowly by boiling alcoholic sodium hydroxide.

Coeroxene, $C_{20}H_{12}O$, formed by boiling coeroxenol with hydriodic acid of sp. gr. 1·6 and phosphorus, crystallises in yellow leaflets, melts at 153°, is readily soluble in chloroform, benzene, or light petroleum, forming solutions with intense yellowish-green fluorescence, and with sulphuric acid gives a red coloration, becoming violet on heating; it is insoluble in aqueous sodium hydroxide and is not oxidised by air, but on treatment with arsenic, nitric, or chromic acid in glacial acetic acid solution forms coeroxonium salts. It is probably identical with R. Meyer and Saul's compound, formed by distilling fluoran with zinc dust (Abstr., 1893, i, 220).

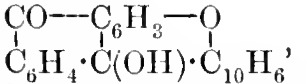
[With MATEI SASSU.]—10-Phenylcoeroxene,  pre-pared by the action of magnesium phenyl bromide on coeroxonol ethyl ether, is orange-red, melts at 188°, at higher temperatures forms a fluorescent vapour, gives an orange coloration with sulphuric acid, and is stable towards feeble oxidising agents, but is oxidised, becoming scarlet, by lead dioxide or chromic or sulphuric acid in hot glacial acetic acid solution.

[With EDUARD LAUBE.]—1-Phenoxyanthraquinone, melting at 145°, is oxidised by sulphur trioxide in sulphuric acid solution at 160—180°, forming coeroxonium sulphate.

1-β-*Naphthoxyanthraquinone*, $C_{24}H_{14}O_3$, prepared by fusing β-naphthol with sodium α-anthraquinonesulphonate and potassium hydroxide at 170—180°, forms small, yellow crystals, melts at about 180°, gives with concentrated sulphuric acid an olive-green coloration, becoming scarlet at 100°, and when heated with 65—70 per cent. sulphuric acid at 130—150° is converted into *β-benzocoeroxonium sulphate*, which is only sparingly soluble. The *ferrichloride*,



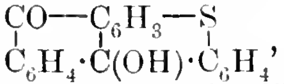
is obtained as a black, crystalline precipitate, which melts and decomposes at 240°, and becomes blood-red when heated with concentrated sulphuric acid at 100°. The *chloride* and *nitrate* form red needles; the *iodide* is obtained as a dark violet, crystalline powder; the *platinichloride* is scarlet.

β-Benzocoeroxonol,  $\begin{array}{l}CO\text{---}C_6H_3\text{—}O \\ C_6H_4\cdot C(OH)\cdot C_{10}H_6\end{array}$, is readily oxidised by air; the *ethyl* ether, $C_{26}H_{18}O_3$, forms almost colourless crystals and melts at 193—194°. *β-Benzocoeroxenol*, $C_{24}H_{14}O_2$, is yellowish-red, forms solutions with strong yellowish-red fluorescence, and is readily oxidised by air. The *acetyl* derivative, $C_{26}H_{16}O_3$, forms yellowish-brown crystals, melts at 206°, and is hydrolysed on prolonged boiling with alcoholic sodium hydroxide. When reduced with concentrated hydriodic acid, β-benzocoeroxonium salts yield *β-benzocoeroxene*, which is strongly fluorescent and is insoluble in aqueous alkali hydroxides.

α-Benzocoeroxonium sulphate is formed by oxidation of 1-*α-naphthoxyanthraquinone*, melting at 275—276°. The members of this series closely resemble the derivatives of β-benzocoeroxene.

[With AUGUST WUERSCH.]—1-*Phenylthioanthraquinone*, $C_{14}H_7O_2\cdot SPh$, prepared by heating thiophenol with potassium hydroxide and potassium α-anthraquinonesulphonate at 170°, crystallises in long, yellow needles, melts at 185°, dissolves in concentrated sulphuric acid, forming a dark green solution, and yields 1-hydroxyanthraquinone when heated with dilute alkali hydroxides. When heated with 70 per cent. sulphuric acid at 160°, it is converted into the sparingly soluble, dark violet *coerthionium sulphate*. *Coerthionium ferrichloride*, $C_{20}H_{11}OSFeCl_4$, forms dark violet crystals, melts and decomposes at 227°, and is decomposed by water. The colour of these thionium salts is darker and more intense than that of the coeroxonium salts.

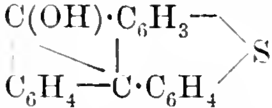
Coerthionol,



$$\begin{matrix} CO-C_6H_3-S \\ C_6H_4\cdot C(OH)\cdot C_6H_4 \end{matrix}$$

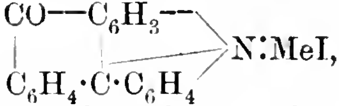
, crystallises in slightly yellow prisms, melts at 220°, and dissolves in dilute acids, forming violet solutions.

Coerthienol,



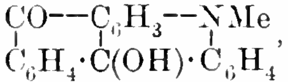
S, formed by reduction of coerthionol, is yellow, dissolves in ether or alcohol, forming a solution with intense green fluorescence, and is readily oxidised to coerthionium salts.

[With CARL SCHENK.]—Coeramidonine (Damman and Gattermann, Abstr., 1902, i, 795), melting at 206°, is formed in good yield by heating *o*-acridylbenzoic acid with fuming sulphuric acid; it dissolves in concentrated sulphuric acid to a blood-red, in glacial acetic acid to a yellow, or in pyridine to a golden solution. *Coeramidonium platinichloride*, $C_{40}H_{24}O_2N_2PtCl_6$, forms glistening, red crystals and melts at 260°; the *picrate*, $C_{26}H_{14}O_8N_4$, forms red crystals and melts at 241°. The *methosulphate* of *N*-methylcoeramidonium, formed by the action of methyl sulphate on coeramidonine, crystallises in small, red leaflets and dyes cotton wool mordanted with tannin a brownish-red, fast to soap. The *picrate*, $C_{27}H_{16}O_8N_4$, forms red crystals and melts at 208°; the *methiodide*,



crystallises in brownish-red needles and melts and evolves methyl iodide at 218°; the *nitrate* melts at 188—189°.

N-Methylcoeramidonol,

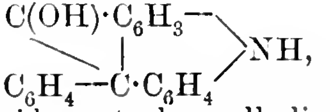


$$\begin{matrix} CO-C_6H_3-NMe \\ C_6H_4\cdot C(OH)\cdot C_6H_4 \end{matrix}$$

, formed by treatment of the quaternary salts with sodium hydroxide, is obtained as a voluminous precipitate, crystallises from alcohol, and melts at 126°. The *ethyl* ether forms small plates and melts at 152°; the *methyl* ether crystallises in small, deep brown leaflets with metallic lustre and melts at 155°.

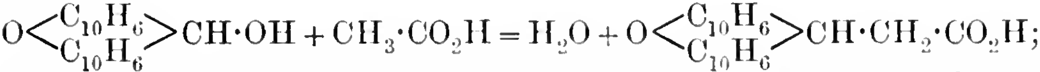
[With ENOS FERRARIO.]—Coeramidonium salts are formed also by the action of fuming sulphuric acid on the acridine derivatives described by Decker and Hock (Abstr., 1904, i, 450).

[With MATEI SASSU.]—*Coeramidenol*,



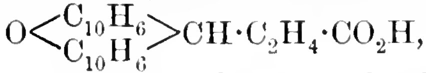
, is prepared by reduction of coeramidonine in acid, neutral, or alkaline solution; it forms a dark red solution with reddish-yellow fluorescence in ether or benzene, is soluble in aqueous alkali hydroxides, but insoluble in dilute sulphuric acid, and is readily oxidised by air. The *acetyl* derivative, $C_{22}H_{15}O_2N$, forms dark red crystals, melts at 254°, has an intense yellow fluorescence in solution, and is hydrolysed by boiling aqueous alkali hydroxides. G. Y.

A Reaction of some Acid Anhydrides. New Series of Acids containing the Pyran Ring. Robert Fosse (*Compt. rend.*, 1906, **143**, 59—61).—Dinaphthapyranol and xanthydrol react with certain acid anhydrides with the elimination of water and the formation of the corresponding substituted acid; thus dinaphthapyranol and acetic anhydride give dinaphthapyrylacetic acid according to the equation



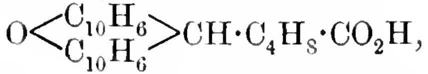
$$O<\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}>CH\cdot OH + CH_3\cdot CO_2H = H_2O + O<\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}>CH\cdot CH_2\cdot CO_2H;$$

and the following acids were thus prepared: *dinaphthapyrylacetic acid*, $O<\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}>CH\cdot CH_2\cdot CO_2H$, forms beautiful, colourless crystals melting at 194° and yields crystalline *silver*, *potassium*, *sodium*, *barium*, and *calcium* salts; *dinaphthapyrylpropionic acid*,



$$O<\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}>CH\cdot C_2H_4\cdot CO_2H,$$

forms colourless crystals which melt at 197°; *dinaphthapyryl-α-iso-butyric acid*, $O<\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}>CH\cdot C_3H_6\cdot CO_2H$, forms colourless crystals melting at 221°; *dinaphthapyryl*iso*valeric acid*,



$$O<\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}>CH\cdot C_4H_8\cdot CO_2H,$$

forms colourless crystals which melt and decompose at 208—210°; *dinaphthapyrylsuccinic acid*, $O<\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}>CH\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H$, forms beautiful, colourless crystals which melt and decompose at 225—230°; *xanthylacetic acid*, $O<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>CH\cdot CH_2\cdot CO_2H$, crystallises in beautiful, colourless needles which melt at 155·5—156°, can be sublimed, and is soluble in alcohol and slightly so in boiling water; and *xanthyl*iso*valeric acid*, $O<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>CH\cdot C_4H_8\cdot CO_2H$, forms colourless crystals which melt at 147—150°. M. A. W.

Stable Derivatives of the Active Base of the Extract of Suprarenal Glands. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 167317).—When one mol. of the active base of the suprarenal glands is combined in aqueous solution with either boric acid (1·5 mols.) or one of its aryl derivatives (phenylboric or *m*-tolylboric acid), a stable soluble salt is produced which, on evaporation, is left as a brittle, vitreous mass having the composition $C_{18}H_{27}O_{11}N_2B_3$; when precipitated with alcohol, the salt contains one H_2O less, but both preparations have the same physiological action. The salts with phenyl- and *m*-tolyl-boric acids are pale yellow powders having similar properties. These compounds may be heated to 250°

without decomposition, and they all give a violet coloration with ferric chloride, which changes to green when this reagent is added in excess.
G. T. M.

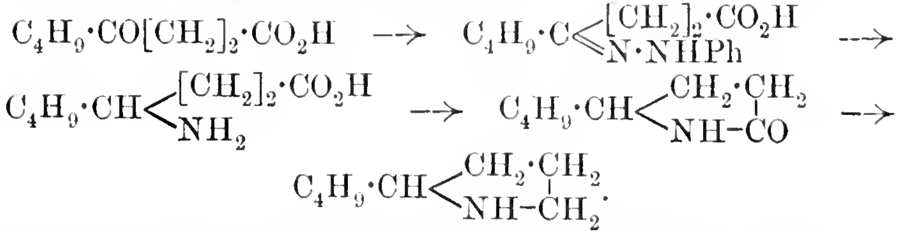
isoConiine and the Synthesis of Coniine. Albert Ladenburg (*Ber.*, 1906, **39**, 2486—2491. Compare Abstr., 1893, i, 442; 1897, i, 173; Wolffenstein, Abstr., 1894, i, 627; 1895, i, 253; 1896, i, 631).—Attempts to obtain *iso*coniine as an individual substance have been unsuccessful, but it has undoubtedly a higher rotatory power than coniine. The fact that synthetic coniine has a greater rotatory power than the purest natural *d*-coniine is probably due to the presence of *iso*coniine in the former. The author has therefore repeated his former experiments and has shown that synthetic coniine is isomeric with *d*-coniine, being identical with it in most of its properties, but having a greater rotatory power, about 4°. It boils at 167° (corr.) and has a sp. gr. 0·8472 at 17° and 0·8445 at 20°; the anhydrous bitartrate melts at 54—55°, the hydrochloride at 221—222°, and the anhydrous platinichloride at 174°. In order to complete the synthesis of *d*-coniine it is necessary to heat the synthetic product for many hours at 290°, when pure *d*-coniine is obtained, having $[\alpha]_D$ 15·67° at 21°.

The allylpyridine required in the synthesis is obtained by heating *a*-picoline, aldehyde, and water at 150°; the resulting aldol compound, $C_5NH_4\cdot CH_2\cdot CHMe\cdot OH$, is heated with concentrated hydrochloric acid at 185°, whereby a mixture of allylpyridine and chloropropylpyridine is obtained, which is reduced to *i*-coniine by sodium and absolute alcohol.
C. S.

[*apo*Morphine Salts.] J. D. Riedel (D.R.-P. 167879. Compare Pschorr, Abstr., 1905, i, 658).—*apo*Morphine methobromide, methochloride, and methonitrate may be produced by adding saturated aqueous solutions of potassium bromide, chloride, and nitrate respectively to the syrupy product of the action of methyl sulphate on *apo*morphine in ethereal solution; the methobromide, which at first is viscid, is rendered crystalline by dissolving in methyl alcohol and precipitating from this solution with acetone.
G. T. M.

Soluble Double Salt of Sodium Salicylate and Barium Theobromine. Aktien-Gesellschaft für Anilin-Fabrikation (D.R.-P. 167140).—Two mols. of sodium salicylate added to a mixture of sodium theobromine (2 mols.) and barium salicylate (1 mol.) in aqueous solution give rise to a soluble *double salt* which separates on concentrating the solution under diminished pressure.
G. T. M.

The Relations between Functional (Reactive) Groups in Remote Positions. Cyclic Imines. Edmond E. Blaise and Houillon (*Compt. rend.*, 1906, **142**, 1541—1543).—The existence of decamethyleneimine (compare Phookan and Krafft, Abstr., 1892, 1180) affording evidence in favour of the view that there exists a periodicity in the closing of heterocyclic chains, the authors attempted to prepare octomethyleneimine by the action of heat on octomethylenediamine hydrochloride. The product obtained by this reaction was a 2-*butylpyrrolidine*, $C_4H_9\cdot CH<\begin{array}{l}NH-CH_2\\ CH_2\cdot CH_2\end{array}$, which has an odour closely resembling that of coniceine and boils at the same temperature as *i*-coniceine; the *platinichloride* melts at 123°, the *aurichloride* at 89°, and the *carbamide* at 152°. 2-Butylpyrrolidine prepared as above is identical with the synthetical compound obtained from β-butyrylpropionic acid [δ-propyl-lævulic acid or γ-keto-octoic acid] by the following series of reactions:



$$C_4H_9\cdot CO[CH_2]_2\cdot CO_2H \longrightarrow C_4H_9\cdot C<\begin{array}{l}[CH_2]_2\cdot CO_2H\\ N\cdot NHPh\end{array} \longrightarrow$$
$$C_4H_9\cdot CH<\begin{array}{l}[CH_2]_2\cdot CO_2H\\ NH_2\end{array} \longrightarrow C_4H_9\cdot CH<\begin{array}{l}CH_2\cdot CH_2\\ NH-CO\end{array} \longrightarrow$$
$$C_4H_9\cdot CH<\begin{array}{l}CH_2\cdot CH_2\\ NH-CH_2\end{array}.$$

In view of the fact that octomethylenediamine hydrochloride on heating suffers an intramolecular migration with the formation of a pyrrolidine base, the authors suggest that Phookan and Krafft's (*loc. cit.*) decamethyleneimine is probably 2-hexylpyrrolidine.

M. A. W.

Constitution of Hæmopyrrole. William Küster [with Karl Haas] (*Annalen*, 1906, **346**, 1—27).—Since hæmatin on oxidation yields a substituted maleimide, it was to be expected that hæmopyrrole would yield an acid amide from the nature of which the constitution of hæmopyrrole could be deduced. Recent investigation of hæmatic acid (Küster) appears to show that hæmopyrrole is either methylpropylpyrrole or 3 : 4-diethylpyrrole, or possibly a mixture of the two.

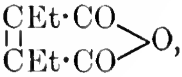
The oxidation of hæmopyrrole yielded no definite results, although the products resembled a di-substituted maleimide and gave a barium salt similar to barium methylethylmaleate. A crystalline imide, soluble in ether and melting at 63°, was also isolated; methylpropylmaleimide melts at 56—57°. Hydrolysis of the imide yielded an oily anhydride, resembling in odour a disubstituted maleic anhydride; but the substance could not be purified.

Methylpropylmaleic anhydride, $C_8H_{10}O_3$, is prepared by treating ethyl propylacetoacetate in ethereal solution with an aqueous solution of potassium cyanide and hydrochloric acid; the methylpropylmalic acid which is obtained by hydrolysing the product is then heated with acetic anhydride at 240°; the anhydride is an oil boiling at 241—242° (corr.) under 760 mm. pressure and has a sp. gr. 1·098 at 15°, and $K = 0{\cdot}0073$. Of the corresponding acid, which could not be isolated, the *barium*, *strontium*, and *calcium* salts crystallise in leaflets with H_2O; the *copper* salt and *silver* salts are anhydrous and amorphous.

The *ethyl* ester prepared from the silver salt is an oil decomposing at 190°. An *ammonium* salt of the methylpropylmaleamide,

$$C_8H_{16}O_3N_2,$$

is formed when dry ammonia is passed into an ethereal solution of the anhydride.

Methylisopropylmaleic anhydride, prepared similarly to the compound last described from ethyl *iso*propylacetoacetate, is a pale yellow oil, boiling at 240—242°. The *barium* salt of the corresponding acid, $C_8H_{10}O_4Ba,H_2O$, crystallises in leaflets, the *copper* and *silver* salts are amorphous. Xeronic acid, 

$\begin{matrix}\mathrm{CEt{\cdot}CO} \\ \| \\ \mathrm{CEt{\cdot}CO}\end{matrix}\!\!>\!O$, was prepared by distilling citraconic acid rapidly at 200°; its boiling point was found to be 239—240°.

Methylpropylmaleimide, prepared by heating the anhydride with alcoholic ammonia at 130°, crystallises in needles melting at 56—57°. The corresponding *iso*propyl *compound* is prepared in a similar manner, and is a pale yellow, crystalline solid melting at 44—45°. Attempts to prepare the corresponding xeronimide did not lead to the formation of a crystalline product.

The reduction of methylpropylmaleic anhydride with zinc dust and acetic acid led to the formation of the fumaroid methylpropylsuccinic acid (m. p. 156—158°); reduction with sodium or aluminium amalgam in acid solution gave the same result. The corresponding *methyliso-propylsuccinic acid* is obtained from the corresponding anhydride; it sinters at 165° and melts at 171°.

On reducing hæmin with hydriodic acid in acetic acid solution, hæmopyrrole is formed and isolated by distillation in steam. The distillate is immediately oxidised with chromic acid, and the product isolated by extraction with ether after neutralisation with sodium carbonate. Finally a crystalline substance containing nitrogen was isolated; it melted at 63—64°. The alkaline liquor, which had been extracted with ether, contained a substance melting at 93—96° which had all the properties of hæmatic acid. K. J. P. O.

3-Benzoylpicolinic Acid. ALFRED KIRPAL (*Monatsh.*, 1906, **27**, 371—377. Compare Bernthsen and Mettegang, Abstr., 1887, 737; Meyer, this vol., i, 358).—*3-Benzoylpicolinamide*,

$$COPh{\cdot}C_5NH_3{\cdot}CO{\cdot}NH_2,$$

is formed from the acid by treatment with thionyl chloride and careful addition of the resulting acid chloride to strongly cooled, aqueous ammonia; it crystallises in quadratic plates, melts at 175°, and is hydrolysed only slowly by boiling water. *2-Amino-3-benzoylpyridine*, $NH_2{\cdot}C_5NH_3{\cdot}COPh$, prepared by the action of bromine on the amide in sodium hydroxide solution, crystallises in yellow needles, melts at 145°, and when boiled with sodium nitrite in dilute sulphuric acid solution yields *2-hydroxy-3-benzoylpyridine*, $OH{\cdot}C_5NH_3{\cdot}COPh$; this is formed also by heating 2-hydroxynicotinyl chloride with benzene and aluminium chloride. It crystallises in colourless needles, melts at 149°, and gives a rose coloration with aqueous ferric sulphate.

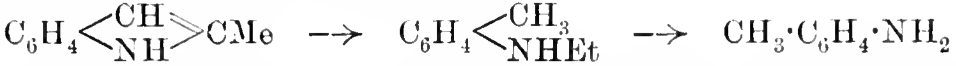
2-Hydroxynicotinyl chloride, $OH{\cdot}C_5NH_3{\cdot}COCl$, prepared by the action of thionyl chloride on the acid, crystallises in short, yellow needles, melts and decomposes at 225°, and loses hydrogen chloride, forming the *anhydride*, on prolonged heating at 100°.

Methyl 2-hydroxynicotinate, $C_6H_4O_3NMe$, prepared by the action of methyl alcohol on the acid chloride or by boiling the acid with methyl alcohol and a few drops of concentrated sulphuric acid, crystallises from benzene in colourless needles and melts at 153°. G. Y.

Formation and Decomposition of the Indole Nucleus by the Catalytic Action of Nickel.

Oreste Carrasco and Maurice Padoa (*Atti R. Accad. Lincei*, 1906, [v], **15**, i, 699—703. Compare this vol., i, 530).—At temperatures up to about 200—250°, and in presence of hydrogen, finely-divided nickel acts as a hydrogenating agent, whilst at higher temperatures the same catalytic agent tends towards dehydrogenation, even when hydrogen itself is present.

Thus, when a mixture of hydrogen and indole vapour is passed over reduced nickel maintained at about 200°, the indole undergoes reduction and loses a carbon atom, forming *o*-toluidine. Under similar conditions, 2-methylindole also yields *o*-toluidine, the changes being probably represented by the scheme:



$$C_6H_4<\begin{matrix}CH\\NH\end{matrix}>CMe \rightarrow C_6H_4<\begin{matrix}CH_3\\NHEt\end{matrix} \rightarrow CH_3{\cdot}C_6H_4{\cdot}NH_2$$

On the other hand, when the vapour of methyl-*o*-toluidine is passed over finely-divided nickel heated at 300—330°, it undergoes de-methylation and gives rise to indole; no indoline is formed in this reaction. T. H. P.

Preparation of Indoxyl and its Homologues.

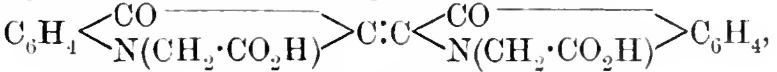
Léon Lilienfeld (D.R.-P. 166447).—The aromatic glycines when condensed with the alkali hydroxides furnish only a very poor yield of indoxyl. An intimate mixture of potassium glycinate with dry potassium hydroxide and calcium hydroxide or magnesia is heated at 150—300° in a current of ammonia. The yield of indoxyl is in this way increased from 10 to 35 or 40 per cent., depending on the way in which the gas is introduced into the fused mass; the more intimate the mixing the higher the yield. G. T. M.

Preparation of Indoxyl.

Badische Anilin- & Soda-Fabrik (D.R.-P. 168292).—Anthranilodiacetic acid,

$$CO_2H{\cdot}C_6H_4{\cdot}N(CH_2{\cdot}CO_2H)_2,$$

is heated for twelve hours with strong sodium hydroxide solution, the mixture then diluted considerably, and oxidised by a current of air until the green colour of the indigotindiacetic acid,



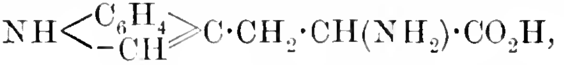
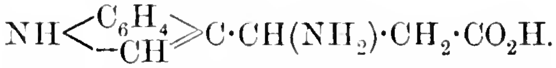
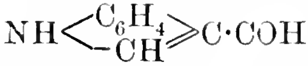
$$C_6H_4<\begin{matrix}CO\\N(CH_2{\cdot}CO_2H)\end{matrix}>C{:}C<\begin{matrix}CO\\N(CH_2{\cdot}CO_2H)\end{matrix}>C_6H_4,$$

changes to the yellowish-red tint of isatinacetic acid,

$$CO<\begin{matrix}CO\\C_6H_4\end{matrix}>N{\cdot}CH_2{\cdot}CO_2H.$$

The last of these compounds is converted into phenylglycine-*o*-carboxylic acid when the solution is evaporated, the product separating in the form of its sodium salt, which can be used in preparing indoxyl and indigotin. G. T. M.

Constitution of the Indole Group in Albumin. III. Oxidation of Tryptophan to Indole-3-aldehyde.

Alexander Ellinger (*Ber.*, 1906, **39**, 2515—2522. Compare Abstr., 1904, i, 639; 1905, i, 827).—It follows from the constitution of Nencki's scatole-acetic acid (indole-3-propionic acid) that tryptophan must be scatole-3-α-aminopropionic,  $NH<\begin{smallmatrix}C_6H_4\\-CH\end{smallmatrix}>C\cdot CH_2\cdot CH(NH_2)\cdot CO_2H$, or scatole-3-$\beta$-aminopropionic acid,  $NH<\begin{smallmatrix}C_6H_4\\-CH\end{smallmatrix}>C\cdot CH(NH_2)\cdot CH_2\cdot CO_2H$. When oxidised by Hopkins and Cole's method (Abstr., 1903, i, 590), tryptophan yields *indole-3-aldehyde*,  $NH<\begin{smallmatrix}C_6H_4\\-CH\end{smallmatrix}>C\cdot COH$, which crystallises in colourless plates, melts at 195°, and when heated with 20 per cent. sulphuric or hydrochloric acid forms a red *dye*; this crystallises in needles, melts at about 175°, and gives a characteristic absorption spectrum resembling, but not identical with, that of the scatole dye from urine. The aldehyde interacts with hippuric acid, sodium acetate, and acetic anhydride, forming an azlactone (compare Erlenmeyer, jun., Abstr., 1902, i, 595), and when oxidised with permanganate in alkaline solution yields indole-3-carboxylic acid.

The action of chloroform and potassium hydroxide in alcoholic solution on indole leads to the formation of indole-3-aldehyde and 3-chloroquinoline (Edinger, Abstr., 1897, i, 103), which boils at 141° under 15 mm. pressure and yields an *aurichloride*, $C_9NH_6Cl,HAuCl_4$, melting at 173°. G. Y.

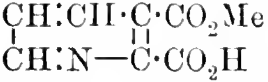
Action of Formaldehyde (Methanal) on Tetrahydroquinoline.

R. A. Weerman (*Rec. trav. chim.*, 1906, **25**, 260—270).—Formaldehyde and tetrahydroquinoline readily condense at the ordinary temperature or on warming to form a yellow oil which probably contains the *aminoalcohol*, $C_9NH_{10}\cdot CH_2\cdot OH$, for on treatment with hydrogen cyanide it yields the *nitrile*, $C_9NH_{10}\cdot CH_2\cdot CN$, in the form of a colourless, thick oil, which boils at 193—195° under 7 mm. pressure, and is saponified by means of an alcoholic solution of sodium hydroxide to form *tetrahydroquinolinoacetamide*, $C_9NH_{10}\cdot CH_2\cdot CO\cdot NH_2$, which crystallises from alcohol in white needles melting at 153—154°. Tetrahydroquinolinoacetonitrile can also be prepared by the method of Knoevenagel (Abstr., 1904, i, 989), by heating a mixture of tetrahydroquinoline, formaldehyde, and sodium hydrogen sulphite, and treating the resulting crystalline acid with potassium cyanide.

If the yellow oil obtained by the condensation of tetrahydroquinoline and formaldehyde is kept, it becomes crystalline, and the chief product is *di-1-tetrahydroquinolylmethane*, $CH_2(C_9NH_{10})_2$, which crystallises from ether or light petroleum in large, rhombic prisms melting at 61—62°, and is converted by the action of mineral acids into the isomeride *di-6-tetrahydroquinolylmethane*, $CH_2(C_9NH_{10})_2$; this base crystallises from ether or absolute alcohol in yellow needles, and melts at 130°, the *hydrochloride*, $C_{19}H_{22}N_2,2HCl$, melts and decomposes at 255°, and the *benzenesulphonyl* derivative,

$$C_{19}H_{20}N_2(SO_2Ph)_2,$$

crystallises from alcohol or acetone in needles and melts at 185—186°. In addition to ditetrahydroquinolylmethane there is also formed a small quantity of a third *isomeride*, $C_{19}H_{22}N_2$, which is sparingly soluble in ether and forms thin, prismatic needles, which melt at 120° and yield formaldehyde when heated with dilute sulphuric acid; its constitution is at present undetermined. M. A. W.

Quinolinic Esters. ALFRED KIRPAL (*Monatsh.*, 1906, **27**, 363—369. Compare Abstr., 1900, i, 51; 1901, i, 227; Wegscheider, Abstr., 1898, i, 30).—The mother liquor from the preparation of 2-methyl-3-hydrogen quinolinate by the action of methyl alcohol on the anhydride, contains a very small quantity of 3-methyl-2-hydrogen quinolinate,  $\begin{array}{l}\mathrm{CH{:}CH\cdot C\cdot CO_2Me} \\ \mathrm{CH{:}N{-}C\cdot CO_2H}\end{array}$; this crystallises from benzene in colourless, transparent, rhombic plates [$a:b:c=0·5928:1:0·5869$], melts at 106°, and decomposes, forming carbon dioxide and ethyl nicotinate, at 120°. It is readily soluble in the ordinary solvents, is hydrolysed only very slowly by boiling water, and forms a *copper* salt crystallising in violet-blue prisms and closely resembling copper nicotinate. A table is given showing the reactions of picolinic and nicotinic acids and of 3-methyl 2-hydrogen and 2-methyl 3-hydrogen quinolinates with a number of metallic salts.

3-Methyl 2-hydrogen quinolinate dissolves in concentrated aqueous ammonia, forming *ammonium 3-quinolinamate*,

$$NH_2\cdot CO\cdot C_5NH_3\cdot CO_2NH_4;$$

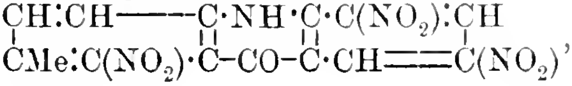
the *acid*, $C_7H_6O_3N_2$, crystallises in colourless prisms and melts at 160°, losing ammonia and forming *quinolinimide*, melting at 230°. G. Y.

1:3:6-Trinitro-7-methylacridone. SALVATORE CUTTITTA (*Gazzetta*, 1906, **36**, i, 325—332).—2-o-*Nitro*-p-*toluidino*-3:5-*dinitrobenzoic acid*, $CO_2H\cdot C_6H_2(NO_2)_2\cdot NH\cdot C_6H_3Me\cdot NO_2$, prepared by the action of alcoholic ammonia on a mixture of 2-chloro-3:5-dinitrobenzoic acid (1 mol.) and *o*-nitro-*p*-toluidine (1 mol.), crystallises from aqueous alcohol with $2\frac{1}{2}H_2O$ in shining, lemon-yellow plates melting at 232° and dissolves sparingly in water or acetic acid and, to a less extent, in benzene. The *ammonium* salt forms golden-yellow laminæ melting at 220° and dissolves in water, benzene, alcohol, or xylene. The *sodium* salt ($+2\frac{1}{2}H_2O$) forms small, orange-red, triclinic crystals [F. RANFALDI: $a:b:c=1·52579:1:0·94494$; $\alpha=76°11'$; $\beta=81°27'$; $\gamma=93°29'$], readily soluble in water or alcohol. The *pyridine* salt,

$$C_{14}H_{10}O_8N_4,C_5NH_5,$$

separates from alcohol in shining, brick-red, triclinic crystals with blue reflex [F. RANFALDI: $a:b:c=1·35414:1:1·09430$; $\alpha=87°16'$; $\beta=76°36'$; $\gamma=92°14'6''$], which melt at 200° and dissolve sparingly in benzene or water.

1:3:6-*Trinitro-7-methylacridone*,



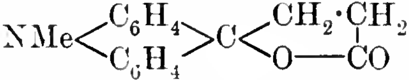
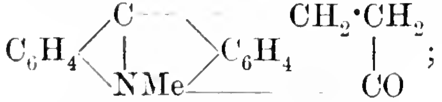
$$\begin{array}{l}\mathrm{CH{:}CH{-\!\!-\!\!-}C\cdot NH\cdot C\cdot C(NO_2){:}CH} \\ \mathrm{CMe{:}C(NO_2)\cdot C{-}CO{-}C\cdot CH{=\!=}C(NO_2)}\end{array},$$

prepared by the action of concentrated sulphuric acid on 2-*o*-nitro-*p*-toluidino-3 : 5-dinitrobenzoic acid, crystallises from acetic acid in shining, yellow plates melting at 320° and dissolves sparingly in benzene or ether and readily in xylene. Its *sodium* salt $(+2\frac{1}{2}H_2O)$ crystallises from alcohol in minute, carmine needles soluble in sodium carbonate solution and is decomposed by water in the cold ; on heating, it deflagrates violently. T. H. P.

Transformations of the Quaternary Ammonium Hydroxides of Acridylpropionic Acid.

CARL SCHENCK (*Ber.*, 1906, 39, 2424—2427. Compare Decker and Hock, Abstr., 1904, i, 450, 620).—5-Acridyl-β-propionic acid (Volpi, Abstr., 1893, i, 350) becomes brown and melts at 310°, and loses carbon dioxide when heated with zinc chloride at 250°. The *methyl* ester, $C_{17}H_{15}O_2N$, formed by boiling the acid with hydrogen chloride in methyl-alcoholic solution, melts at 95°, is hydrolysed slowly by boiling aqueous sodium hydroxide, and forms salts which are decomposed by water. The *iodide* forms orange needles and melts and decomposes at 205° ; the *picrate*, $C_{23}H_{18}O_9N_4$, crystallises in glistening, yellow plates and melts at 222°. When heated with methyl sulphate at 120°, the *N*-atom of the methyl ester is methylated and the resulting *base* forms a quaternary *methosulphate* ; this yields a quaternary *picrate*, $C_{24}H_{20}O_9N_4$, which crystallises from alcohol, melts at 210°, and is not decomposed by water, alcohol, or sodium hydrogen carbonate.

Ethyl 5-acridyl-β-propionate, $C_{18}H_{17}O_2N$, crystallises in long needles, melts at 83°, and is more readily hydrolysed than the methyl ester ; the picrate, $C_{24}H_{20}O_9N_4$, melts at 192°.

The hydrolysis of the quaternary salts of the methylacridylpropionic esters by means of aqueous sodium hydroxide leads to the formation of the colourless, crystalline *lactone*,  $NMe{<}\begin{matrix}C_6H_4\\C_6H_4\end{matrix}{>}C{<}\begin{matrix}CH_2\cdot CH_2\\|\qquad|\\O—CO\end{matrix}$, which is soluble in ether, benzene, or alcohol, and readily dissolves in water or dilute alkali hydroxides, changing into the yellow, fluorescent *betaine*,  $C_6H_4{<}\begin{matrix}C\\|\\NMe\end{matrix}{>}C_6H_4\quad\begin{matrix}CH_2\cdot CH_2\\|\\CO\end{matrix}$; the *hydrochloride*, $C_{17}H_{16}O_2NCl$, formed by dissolving the lactone in hot dilute hydrochloric acid, crystallises in rosettes and melts and decomposes at 260°.

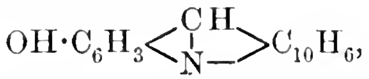
A *base*, which may be diacridylethane, is formed together with acridylpropionic acid by fusing diphenylamine with succinic acid ; it forms yellow crystals, melts at about 92°, gives a yellow, fluorescent solution with concentrated sulphuric acid, and forms reddish-violet salts with mineral acids ; the *picrate* melts at 113—114°. G. Y.

Derivatives of 5-Phenylacridine. III. 5-*p*-Bromophenylacridine.

ALBERT E. DUNSTAN and JAMES A. STUBBS (*Ber.*, 1906, 39, 2402—2404. Compare Dunstan and Oakley, this vol., i, 383).—5-*p*-Bromophenylacridine, $C_{13}H_8N\cdot C_6H_4Br$, prepared by heating *p*-bromobenzoic acid with diphenylamine and zinc chloride at 220—230°, forms greenish-yellow, prismatic crystals, melts at 234°, and dissolves in benzene, toluene, xylene, or acetic acid, less readily in methyl or ethyl alcohol, forming fluorescent solutions. The *chromate*, $(C_{19}H_{12}NBr)_2,H_2CrO_4$, the yellow *platinichloride*, $(C_{19}H_{12}NBr)_2,H_2PtCl_6$, the *hydrochloride*, which crystallises in green leaflets and melts at 267°, and the *nitrate*, which forms olive-green leaflets and melts at 172°, were prepared. The *methiodide*, $C_{20}H_{15}NBrI$, prepared by the action of methyl iodide on the acridine, forms small, dark red crystals and melts and decomposes at 240°. G. Y.

Conversion of *o*-Nitro- and *op*-Dinitro-benzyl Chlorides into Acridine Derivatives. Carlo Baezner and J. Gueorguieff (*Ber.*, 1906, **39**, 2438—2447. Compare Baezner, Abstr., 1904, i, 928).—The *acetyl* derivative of 10-amino-1 : 2-phenonaphthacridine, $C_{19}H_{14}ON_2$, crystallises in yellow needles, melts at 267°, and dissolves in alcohol, forming an orange-yellow solution with violet fluorescence; the *hydrochloride* is yellow; the *platinichloride*, $(C_{17}H_{12}N_2)_2,H_2PtCl_6$, forms reddish-brown crystals; the *zincichloride*, $(C_{17}H_{12}N_2),H_2ZnCl_4$, forms slender, red needles; the *chromate* is brownish-red and is insoluble. In solution the salts are yellow and have a green fluorescence.

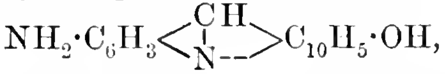
10-*Hydroxy*-1 : 2-*phenonaphthacridine*,



$OH\cdot C_6H_3<\begin{smallmatrix}CH\\ |\\ N\end{smallmatrix}>C_{10}H_6$,

formed by heating the 9-amino-compound with 10 per cent. sulphuric acid in a sealed tube at 200—210°, crystallises from nitrobenzene in small, yellow needles, melts at about 300—301°, is soluble in aqueous alkali hydroxides, and dissolves in concentrated sulphuric acid or alcohol, forming a yellow solution with green fluorescence. The *hydrochloride*, $C_{17}H_{12}ONCl$, and the *sodium* salt, $C_{17}H_{10}ONNa$, are described. The *acetyl* derivative, $C_{19}H_{13}O_2N$, crystallises in white needles, melts at 160°, and has a violet fluorescence in alcoholic solution. The *benzoyl* derivative, $C_{24}H_{15}O_2N$, crystallises in small, yellow needles, melts at 186·5—187°, and dissolves in concentrated sulphuric acid, forming a solution with green, in alcohol forming a solution with violet, fluorescence.

10-*Amino*-5-*hydroxy*-1 : 2-*phenonaphthacridine*,



$NH_2\cdot C_6H_3<\begin{smallmatrix}CH\\ |\\ N\end{smallmatrix}>C_{10}H_5\cdot OH$,

is formed together with a brownish-red *substance*, which is insoluble in aqueous alkali hydroxides, by the action of stannous chloride and concentrated hydrochloric acid on 2 : 4-dinitrobenzyl chloride and 2 : 7-dihydroxynaphthalene; it crystallises from nitrobenzene in small, orange-yellow needles, melts at 180°, and dissolves in benzene or toluene, forming a yellow solution with bluish-green, in alcohol forming an orange-red solution with green fluorescence, or in mineral acids forming red solutions. The *hydrochloride*, $C_{17}H_{13}ON_2Cl$, dyes cotton-wool mordanted with tannin orange-brown. The *acetyl* derivative, $NHAc\cdot C_{17}H_9N\cdot OH$, crystallises from nitrobenzene in small, yellow needles, melts at 283—285°, and dissolves in aqueous alkali hydroxides. The *dibenzoyl* derivative, $C_{31}H_{20}O_3N_2$, forms small, bronze-yellow needles, melts at 212—215°, is insoluble in aqueous alkali hydroxides, and forms solutions in organic solvents with green to violet-blue fluorescence.

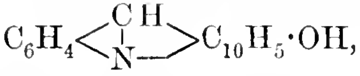
5 : 10-*Dihydroxy*-1 : 2-*phenonaphthacridine*, formed by heating 10-amino-5-hydroxy-1 : 2-phenonaphthacridine with 10 per cent. sulphuric acid in a sealed tube at 190—205°, is soluble only in aqueous alkali hydroxides; the *dibenzoyl* derivative, $C_{31}H_{19}O_4N$, melts at 198—201°.

5 : 10-*Diamino*-1 : 2-*phenonaphthacridine*,

$$NH_2\cdot C_6H_3{<}\genfrac{}{}{0pt}{}{CH}{N}{>}C_{10}H_5\cdot NH_2,$$

formed together with 10-amino-5-hydroxy-1 : 2-phenonaphthacridine from 2 : 4-dinitrobenzyl chloride and 7-acetylamino-2-naphthol, crystallises in light brown needles, melts at 180°, forms fluorescent solutions, and dyes cotton-wool mordanted with tannin brownish-red.

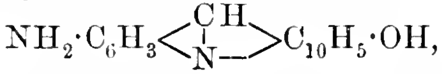
[With A. GARDIOL.]—4-*Hydroxy*-1 : 2-*phenonaphthacridine*,



$$C_6H_4{<}\genfrac{}{}{0pt}{}{CH}{N}{>}C_{10}H_5\cdot OH,$$

formed from *o*-nitrobenzyl chloride and 2 : 6-dihydroxynaphthalene, melts at 212°, is readily soluble in nitrobenzene, glacial acetic acid, or, forming a yellow solution, in dilute sodium hydroxide. The *hydrochloride*, $C_{17}H_{12}ONCl$, was analysed.

10-*Amino*-4-*hydroxy*-1 : 2-*phenonaphthacridine*,



$$NH_2\cdot C_6H_3{<}\genfrac{}{}{0pt}{}{CH}{N}{>}C_{10}H_5\cdot OH,$$

formed from 2 : 4-dinitrobenzyl chloride and 2 : 6-dihydroxynaphthalene, crystallises from nitrobenzene in microscopic, yellowish-brown needles and melts at 218—220°. The *hydrochloride*, $C_{17}H_{12}ON_2,HCl$, melts at 168°. The *acetyl* derivative melts at 263°.

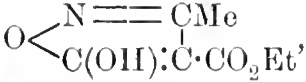
10-*Amino*-1-*methoxy*-1 : 2-*phenonaphthacridine*,

$$NH_2\cdot C_6H_3{<}\genfrac{}{}{0pt}{}{CH}{N}{>}C_{10}H_5\cdot OMe,$$

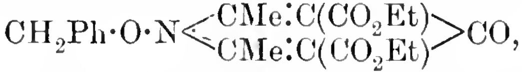
is formed from 2 : 4-dinitrobenzyl chloride and 2-*hydroxy*-3-*methoxynaphthalene*, which is prepared by the action of methyl sulphate on 2 : 3-dihydroxynaphthalene, crystallises in white needles, melts at 65°, and boils at about 285°. The condensation product is isolated as the *acetyl* derivative, $C_{20}H_{16}O_2N_2$, which melts at 187°, and on hydrolysis with concentrated hydrochloric acid yields the free *base*. This melts at 137°, gives an orange-brown coloration and green fluorescence with concentrated sulphuric acid, dissolves in ether or hot alcohol, forming a solution with green fluorescence, and yields a *hydrochloride* melting at 212°. G. Y.

Existence of *iso*Pyrophthalone. ALEXANDER EIBNER and M. LÖBERING (*Ber.*, 1906, **39**, 2447—2450. Compare Abstr., 1903, i, 644; 1904, i, 921; von Huber, Abstr., 1903, i, 576).—Pyrophthalone, obtained from phthalic anhydride and α-picoline at 200°, melts when pure at 287°; the *sodium* derivative, $C_{14}H_8O_2NNa$, is not decomposed by water and separates from a concentrated aqueous solution in a felted mass of red needles. The *bromotribromide*, $C_{14}H_8O_2NBr_4$, forms thick, orange-yellow prisms, and is converted by alcohol, water, and ammonia at the ordinary temperature into *monobromopyrophthalone*, $C_{14}H_8O_2NBr$, which, obtained also by brominating pyrophthalone in glacial acetic acid, or the sodium derivative, crystallises in colourless leaflets, melts at 157°, and is changed into pyrophthalone by prolonged boiling with alcohol and water or ammonia. *Anilpyrophthalone*, $C_{20}H_{14}ON_2$, prepared in benzene solution with aluminium chloride as condensing agent, separates from alcohol in felted, red needles, melts at 185°, and is decomposed by hydrochloric acid; with phenylhydrazine it yields *pyrophthalone phenylhydrazone*, $C_{20}H_{15}ON_3$, which forms reddish-brown needles and melts at 215°.

Von Huber's "*iso*pyrophthalone," obtained from phthalyl chloride and α-picoline and melting at 280°, yields a monobromide and an anil identical with the preceding compounds, and is therefore impure pyrophthalone. From phthalyl chloride and α-picoline in benzene solution the authors have obtained pyrophthalone in the pure state, melting at 287°. C. S.

Action of Hydroxylamine on Ethyl Dimethylpyronedicarboxylate. F. Carlo Palazzo (*Gazzetta*, 1906, **36**, i, 596—611. Compare Abstr., 1904, i, 762).—The author shows that the constitution proposed by him (*loc. cit.*) for the compound $C_7H_9O_4N$, obtained by the action of hydroxylamine on ethyl dimethylpyronedicarboxylate, is erroneous, the true constitution,  $O<\begin{matrix}N{=\!=}CMe\\ C(OH){:}\overset{|}{C}\cdot CO_2Et\end{matrix}$, being that of *ethyl 5-hydroxy-3-methyl*iso*oxazole-4 carboxylate.*

The action of benzylhydroxylamine on ethyl dimethylpyronedicarboxylate differs from that of hydroxylamine, and gives rise to *ethyl 1-benzyloxy-2 : 6-dimethyl-4-pyridone-3 : 5-dicarboxylate*,



$$CH_2Ph\cdot O\cdot N<\begin{matrix}CMe{:}C(CO_2Et)\\ CMe{:}C(CO_2Et)\end{matrix}>CO,$$

which crystallises from ethyl acetate in white, feathery needles and melts at 138°. On boiling with a dilute mineral acid, this compound is transformed into *1-hydroxy-2 : 6-dimethyl-4-pyridone-3 : 5-dicarboxylic acid*, which crystallises from alcohol in slender, white needles melting and decomposing at 245°, and gives an intense, blood-red coloration with ferric chloride. T. H. P.

Nitration of *m*-Diarylsulphondiamides. Aktien-Gesellschaft für Anilin-Fabrikation (D.R.-P. 166600).—The *m*-diarylsulphondiamides are readily nitrated with warm dilute nitric acid, the reaction being accelerated either by efficient stirring or by the addition of an inert solvent for the diamide. The *m*-diarylsulphondiamides are prepared from the *m*-diamines by treating these bases (1 mol.) with the arylsulphonic chloride (2 mols.) in the presence of aqueous sodium carbonate.

s-*Ditoluene*-p-*sulphonyl*-m-*phenylenediamine*, which is obtained in white crystals melting at 172°, yields 4-*nitro*-s-*ditoluene*-p-*sulphonyl*-m-*phenylenediamine*, a brownish-yellow, crystalline substance melting at 169°.

6-*Nitro*-s-*ditoluene*-p-*sulphonyl*-2 : 4-*tolylenediamine*,

$$NO_2\cdot C_6H_2Me(NH\cdot SO_2\cdot C_7H_7)_2,$$

forms yellow crystals and melts at 210°.

4-*Chloro*-s-*ditoluene*-p-*sulphonyl*-m-*phenylenediamine*,

$$C_6H_3Cl(NHSO_2\cdot C_7H_7)_2,$$

separates in white prisms melting at 215°, and yields 4-*chloro*-6-*nitro*-s-*ditoluene*-p-*sulphonyl*-m-*phenylenediamine*, which crystallises in yellow prisms and melts at 196°.

s-*Dibenzenesulphonyl*-2 : 4-*tolylenediamine* crystallises in white needles melting at 191°; its *nitro*-derivative is obtained in yellow prisms and melts at 185°. G. T. M.

A New Method of Preparation and the Properties of Quaternary Hydrazines. HARTWIG FRANZEN and F. ZIMMERMANN (*Ber.*, 1906, **39**, 2566—2569).—*Diphenyldibenzylhydrazine*,

$$C_7H_7\cdot NPh\cdot NPh\cdot C_7H_7,$$

obtained by boiling diphenyldibenzyltetrazone with xylene, is a faintly yellow oil which boils at 181—181·5° under 19 mm. pressure, forms an unstable *hydrochloride*, $C_{26}H_{24}N,2HCl$, which crystallises in white needles and melts at 215·5°, and is decomposed by boiling 2*N*-sulphuric acid into aniline, benzylaniline, and benzaldehyde.

Diphenyldimethyltetrazone is decomposed in boiling xylene, forming ammonia and phenyl *iso*cyanide. C. S.

Acetylated Indophenols. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 168229).—The acetylated indophenol,

$$NHAc\cdot C_6H_4\cdot N\colon C_6H_3Me\colon O,$$

obtained by oxidising an alkaline solution of *p*-aminoacetanilide and *o*-cresol with sodium hypochlorite, is a reddish-brown powder, very soluble in alcohol, which crystallises from hot water in brick-red needles. A similar compound is obtained when phenol is substituted for *o*-cresol. When these substances are warmed with aqueous sodium sulphide they are simultaneously hydrolysed and reduced to leuco-derivatives. G. T. M.

Action of Sulphuryl Chloride on Pyrazole. GIROLAMO MAZZARA and ALESSANDRO BORGO (*Atti R. Accad. Lincei*, 1906, [v], **15**, i, 704—710).—The action of sulphuryl chloride (1 mol.) on an ethereal solution of pyrazole maintained at 0° yields 4-chloropyrazole, which crystallises in the rhombic system [C. VIOLA : $a:b:c = 0·8026:1:0·8284$] and melts at 77° (69—71°, Knorr, Abstr., 1895, i, 396).

4-*Chloro*-1-*methylpyrazole*, $C_3H_2N_2ClMe$, prepared by treating a methyl-alcoholic solution of 4-chloropyrazole with methyl-alcoholic potassium hydroxide and methyl iodide, is a yellow, oily liquid, which boils at 167° under 756 mm. pressure, has a penetrating and irritating odour, and is turned red by the action of light. T. H. P.

Researches on Pyrazolones. New Methods of Synthesis of Pyrazolones. CHARLES MOUREU and I. LAZENNEC (*Compt. rend.*, 1906, **142**, 1534—1537).—Ethyl amylpropiolate, $C_5H_{11}\cdot C\colon C\cdot CO_2Et$, and ethyl hexoylacetate, $C_5H_{11}\cdot CO\cdot CH_2\cdot CO_2Et$, react with phenylhydrazine to form the same phenylamylpyrazolone melting at 96°; similarly, the same phenylhexylpyrazolone melting at 84—85° is obtained by the action of phenylhydrazine on ethyl hexylpropiolate, $C_6H_{13}\cdot C\colon C\cdot CO_2Et$, or on methylheptoylacetate, $C_6H_{13}\cdot CO\cdot CH_2\cdot CO_2Et$ (compare Rothenburg, Abstr., 1893, i, 611); the phenylamylpyrazolone and phenylhexylpyrazolone thus prepared are isomeric with the compounds obtained by the action of phenylhydrazine on ethyl β-ethoxy-β-amylacrylate or ethyl β-ethoxy-β-hexylacrylate, which melt at 280° and 270° respectively.

Hydrazine hydrate condenses with phenylpropiolamide,
$$\mathrm{CPh\!:\!C\cdot CO\cdot NH_2}$$
(this vol., i, 148), or with ethyl β-ethoxy-β-phenylacrylate,
$$\mathrm{OEt\cdot CPh\!:\!CH\cdot CO_2Et},$$
to yield a phenylpyrazolone melting at 237°, which is identical with the compound prepared similarly from ethyl phenylpropiolate or ethyl benzoylacetate (Rothenburg, *loc. cit.*).

Phenylhydrazine reacts with ethyl β-ethoxy-β-phenylacrylate to form a diphenylpyrazolone which melts at 256° and is identical with the compound prepared by Knorr by the action of heat on phenylcinnamoylhydrazine (Abstr., 1887, 665), and isomeric with the diphenylpyrazolone melting at 136°, which is formed by the action of phenylhydrazine on ethyl phenylpropiolate or ethyl benzoylacetate; it is probable that the isomeride melting at 256° is 1 : 5-diphenyl-3-pyrazolone,  $\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot NPh}\\ \mathrm{CH\!:\!CPh}\end{matrix}$, formed by the elimination of $\mathrm{C_2H_5\cdot OH}$ from the intermediate compound, $\mathrm{OEt\cdot CPh\!:\!CH\cdot CO\cdot NH\cdot NHPh}$, and that the isomeride melting at 136° is 2 : 5-diphenyl-3-pyrazolone,  $\mathrm{CO}<\begin{matrix}\mathrm{NPh\cdot NH}\\ \mathrm{CH{=}CPh}\end{matrix}$, similarly formed from the intermediate compound, $\mathrm{NHPh\cdot NH\cdot CPh\!:\!CH\cdot CO_2Et}$ (compare Buchner, Abstr., 1890, 156, and Rothenburg, *loc. cit.*). M. A. W.

Preparation of Cyclic Carbamide Derivatives (Pyrimidines).

Emanuel Merck (D.R.-P. 170555, 170657).—4-Amino-2 : 6-dihydroxypyrimidine is obtained by adding ethyl cyanoacetate to a mixture of acetylcarbamide and sodamide in xylene; the mixture, which is cooled during the addition of the ester, is afterwards heated at 150° for five to six hours, when the product is treated with water and the pyrimidine precipitated with acetic acid.

4-Amino-2 : 6-dihydroxy-3-methylpyrimidine is prepared similarly from acetylmethylcarbamide, sodamide, and ethyl cyanoacetate; the final aqueous extract contains its sodium salt, and the free pyrimidine is precipitated with acetic acid.

The foregoing pyrimidine can also be prepared from the same reagents, using, however, instead of sodamide, a solution of sodium ethoxide in absolute alcohol. G. T. M.

Preparation of 5 : 5-Dialkylbarbituric Acids.

Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 163136. Compare this vol., i, 538).—Dialkylmalonodiamides and alkyl carbonates condense in presence of alkali ethoxides to form 5 : 5-dialkylbarbituric acids; as

$$\mathrm{CEt_2(CO\cdot NH_2)_2 + CO(OEt)_2 = 2EtOH + CEt_2}<\begin{matrix}\mathrm{CO\cdot NH}\\ \mathrm{CO\cdot NH}\end{matrix}>\mathrm{CO}.$$

Alkali hydroxides cannot be substituted for ethoxides, as decomposition then takes place. C. H. D.

Preparation of 5:5-Diethylbarbituric Acid. Aktien-Gesellschaft für Anilin-Fabrikation (D.R.-P. 167332).—Although at 100° diethylmalonamide and carbonyl chloride interact to form large quantities of diethylmalononitrile, whilst the carbamide is not produced, yet when the condensation is carried out at 150° less of the nitrile is formed, whilst a 30 to 40 per cent. yield of the carbamide derivative is obtained. The residue when crystallised from water yields pure diethylbarbituric acid melting at 191°. G. T. M.

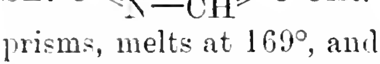
Preparation of Dialkylbarbituric Acids and Dialkyloxypyrimidine Derivatives. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 168406, 168407. See preceding abstracts).—The alkyl or aryl carbonates and dialkylmalonamides condense to form substituted barbituric acids when heated in contact with sodium or sodamide. Thus diethylbarbituric acid may be obtained from ethyl carbonate and diethylmalonamide and dipropylbarbituric acid from phenyl carbonate and dipropylmalonamide.

Diethylthiobarbituric acid may be prepared by heating diethylmalonamide, carbon disulphide, and sodium ethoxide in alcoholic solution at 100°. The product is crystallised from water.

Diethylbarbituric and dipropylbarbituric acids are formed when diethylmalonamide and dipropylmalonamide respectively are heated at 100° with carbon oxysulphide and alcoholic sodium ethoxide.

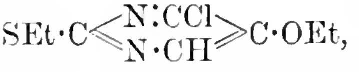
G. T. M.

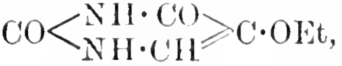
Pyrimidines. Synthesis of *iso*Barbituric Acid and of 5-Hydroxycytosine. Treat B. Johnson and Elmer V. McCollum (*J. Biol. Chem.*, 1906, i, 437—449. Compare Abstr., 1903, i, 526).—A mixture of ethyl formate and ethyl ethylglycollate reacts with sodium suspended in ether, yielding the sodium derivative of *ethyl β-hydroxy-a-ethoxyacrylate*, $NaO\cdot CH{:}C(OEt)\cdot CO_2Et$, which condenses with an aqueous solution of ψ-ethylthiocarbamide hydrobromide and potassium hydroxide, yielding *6-oxy-5-ethoxy-2-ethylthiolpyrimidine*,



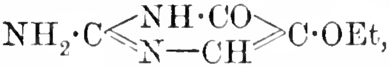
$\mathrm{SEt\cdot C}\left<\begin{matrix}\mathrm{NH\cdot CO}\\ \mathrm{N{-}CH}\end{matrix}\right>\mathrm{C\cdot OEt}$. This crystallises from alcohol in rhombic prisms, melts at 169°, and is only sparingly soluble in hot water. It is not decomposed when boiled with hydrochloric or hydrobromic acid; with 20 per cent. hydrochloric acid at 150° it yields ethyl chloride, ethyl mercaptan, *iso*barbituric acid, and probably 2:6-dihydroxy-5-ethoxypyrimidine. A good yield of *iso*barbituric acid is obtained when the pyrimidine derivative is hydrolysed with concentrated hydrochloric acid at 150°.

6-Chloro-5-ethoxy-2-ethylthiolpyrimidine,



$\mathrm{SEt\cdot C}\left<\begin{matrix}\mathrm{N{:}CCl}\\ \mathrm{N\cdot CH}\end{matrix}\right>\mathrm{C\cdot OEt}$, obtained by the action of phosphorus oxychloride on the corresponding oxypyrimidine, crystallises in colourless prisms, melts at 46°, and distils at 185° under 25 mm. pressure. It forms an additive compound with phosphorus oxychloride, which is decomposed by hot water. Alcoholic ammonia reacts with the chloro-derivative at 150—160°, yielding *6-amino-5-ethoxy-2-ethylthiolpyrimidine*, $C_8H_{13}ON_3S$, which crystallises from hot water in rhombic prisms melting at 105°. The amino-compound is decomposed by 20 per cent. hydrochloric acid at 150—160° into ethyl mercaptan and *iso*barbituric acid, together with the intermediate products 5-ethoxycytosine and 2 : 6-*dioxy-5-ethoxypyrimidine*,  $\mathrm{CO}{<}\begin{matrix}\mathrm{NH\cdot CO}\\ \mathrm{NH\cdot CH}\end{matrix}{>}\mathrm{C\cdot OEt}$, which crystallises from water in radiating prisms, begins to turn brown at 220°, and decomposes at 260—280°. 5-*Ethoxycytosine*,  $\mathrm{CO}{<}\begin{matrix}\mathrm{N{:}C(NH_2)}\\ \mathrm{NH-CH}\end{matrix}{>}\mathrm{C\cdot OEt}$, is readily soluble in warm water, crystallises in slender prisms, and melts at 300°. Its *picrate* melts at 229—231°.

Concentrated hydrochloric acid at 150° transforms the aminoethoxyethylthiolpyrimidine into ethyl chloride, ethyl mercaptan, a small amount of *iso*barbituric acid, and 5-*hydroxycytosine*, the *picrate* of which slowly decomposes above 240°.

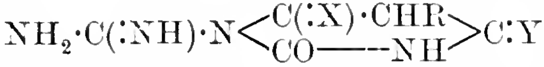
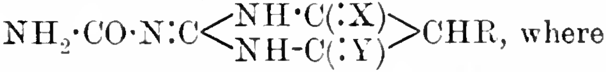
6-*Oxy-5-ethoxy-2-methylthiolpyrimidine* crystallises from alcohol in stout prisms and melts at 190°. 2-*Amino-6-oxy-5-ethoxypyrimidine* or 5-*ethoxy*iso*cytosine*,  $\mathrm{NH_2\cdot C}{<}\begin{matrix}\mathrm{NH\cdot CO}\\ \mathrm{N-CH}\end{matrix}{>}\mathrm{C\cdot OEt}$, obtained by the action of guanidine on ethyl sodio-β-hydroxy-α-ethoxyacrylate, is best purified by precipitation with mercuric chloride. The *sulphate*,

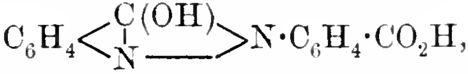
$$(C_6H_9O_2N_3)_2,H_2SO_4,2H_2O,$$

decomposes at 225—226°. The base crystallises from water in microscopic prisms and melts at 248°. J. J. S.

Preparation of Pyrimidine Derivatives. EMANUEL MERCK (D.R.-P. 170586).—Guanylcarbamide, which may have either of the following formulæ, $NH_2\cdot CO\cdot NH\cdot C(NH)\cdot NH_2$ or $NH_2\cdot CO\cdot N{:}C(NH_2)_2$, condenses with either ethyl cyanoacetate or ethyl hydrogen malonate to give a mixture of compounds of the pyrimidine series. The first formula would lead to compounds having the formulæ

$$\mathrm{NH_2\cdot CO\cdot N}{<}\begin{matrix}\mathrm{C({:}X)-CHR}\\ \mathrm{C({:}NH)\cdot NH}\end{matrix}{>}\mathrm{C{:}Y}$$

and  $\mathrm{NH_2\cdot C({:}NH)\cdot N}{<}\begin{matrix}\mathrm{C({:}X)\cdot CHR}\\ \mathrm{CO\text{———}NH}\end{matrix}{>}\mathrm{C{:}Y}$, whilst the second formula for guanylcarbamide would give rise to compounds having the following structure:  $\mathrm{NH_2\cdot CO\cdot N{:}C}{<}\begin{matrix}\mathrm{NH\cdot C({:}X)}\\ \mathrm{NH\text{-}C({:}Y)}\end{matrix}{>}\mathrm{CHR}$, where R = hydrogen or an alkyl group, X and Y either oxygen or an imino-group. G. T. M.

Formation of Indazyl Derivatives from *o*-Hydrazobenzoic Acid. PAUL CARRÉ (*Compt. rend.*, 1906, **143**, 54—56).—The compound, $(C_{14}H_8O_2N_2)_2$, obtained by the action of water on benzaldehyde-*o*-azobenzoic acid (compare Abstr., 1905, i, 307) can be prepared more readily by treating *o*-hydrazobenzoic acid with phosphorus pentachloride (compare Freundler, this vol., i, 544). The compound yields 3-*hydroxy-o-indazylbenzoic acid*,  $\mathrm{C_6H_4}{<}\begin{matrix}\mathrm{C(OH)}\\ \mathrm{N}\text{———}\end{matrix}{>}\mathrm{N\cdot C_6H_4\cdot CO_2H}$, on saponification, and is regenerated from this acid by the action of dehydrating agents; it is therefore a *lactone* of 3-*hydroxy-o-indazylbenzoic acid.*

3-*Hydroxy*-o-*indazylbenzoic acid* crystallises from alcohol in white plates and melts at 228° with formation of the lactone; the *ethyl* ester crystallises from alcohol in white needles, melts at 132°, and decomposes at a slightly higher temperature into the lactone and ethyl alcohol. M. A. W.

N-Aminoheterocyclic Compounds. I. 1-Amino-2-phenyl-2:3-naphthaglyoxaline. Hartwig Franzen (*J. pr. Chem.*, 1906, [ii], 73, 545—569. Compare Abstr., 1905, i, 244, 830).—If 1:3-dibenzylideneamino-2-phenyldihydro-2:3-naphthaglyoxaline is boiled with glacial acetic acid and a small amount of concentrated hydrochloric acid, and the cooled liquid poured into water and distilled in a current of steam, ammonium chloride and 1-benzylideneamino-2-phenyl-2:3-naphthaglyoxaline are formed; if the distillation is continued, the latter substance is further hydrolysed to benzaldehyde and 1-amino-2-phenyl-2:3-naphthaglyoxaline, $C_{10}H_6{<}\begin{smallmatrix}N\\N(NH_2)\end{smallmatrix}{>}CPh$. This crystallises from alcohol in small, slightly brown leaflets, melts and decomposes at 264°, dissolves readily in boiling acetone, and is a mono-acid base. Although containing the group $:N\cdot NH_2$, the properties of the base are entirely different from those of the *as.-sec.*-hydrazines. It reacts only slowly with aromatic aldehydes or phenylthiocarbimide, is not reduced by zinc dust and glacial acetic acid or oxidised when boiled with mercuric oxide and alcohol, does not react with acetone, acetophenone, aliphatic aldehydes, cyanic acid, or sodium and hydrochloric acid, and yields 2-phenyl-2:3-naphthaglyoxaline when boiled with amyl nitrite and concentrated hydrochloric acid in alcoholic solution. The *hydrochloride*, $C_{10}H_6{<}\begin{smallmatrix}N(HCl)\\N(NH_2)\end{smallmatrix}{>}CPh$, crystallises in slightly yellow needles, melts at 245°, and is decomposed by water; the *sulphate*, $(C_{17}H_{13}N_3)_2,H_2SO_4$, forms matted, yellow needles and melts at 240°; the *nitrate*, $C_{17}H_{14}O_3N_4$, crystallises in yellow needles and melts and decomposes at 176°; the *picrate*, $C_{17}H_{13}N_3,C_6H_3O_7N_3$, forms small, yellow needles and melts and decomposes at 205—206°; the *platinichloride*, $(C_{17}H_{13}N_3)_2,H_2PtCl_6$, is obtained as a yellow precipitate.

1-*Acetylamino*-2-*phenyl*-2:3-*naphthaglyoxaline*,

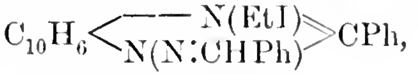
$$C_{10}H_6{<}\begin{smallmatrix}N\\N(NHAc)\end{smallmatrix}{>}CPh,$$

formed by boiling the base with acetic anhydride, crystallises in stout, colourless prisms and melts at 192°. 1-*Phenylthiocarbamido*-2-*phenyl*-2:3-*naphthaglyoxaline*, $C_{11}H_6N_2Ph\cdot NH\cdot CS\cdot NHPh$, formed by prolonged boiling of the amino-base with phenylthiocarbimide in alcoholic solution, crystallises in slender, yellow needles and is only sparingly soluble in boiling alcohol. The *ethiodide*, $C_{10}H_6{<}\begin{smallmatrix}N(EtI)\\N(NH_2)\end{smallmatrix}{>}CPh$, prepared by boiling the base with ethyl iodide in alcoholic solution in a reflux apparatus, crystallises in rosettes of slender, yellow needles, melts and blackens at 195—196°, and when heated with dilute hydrochloric acid is decomposed, forming 1-amino-2-phenyl-2:3-naphthaglyoxaline hydrochloride.

1-*Benzylideneamino-2-phenyl-2 : 3-naphthaglyoxaline*,

$$C_{10}H_6<\begin{array}{l}\text{————}N\\ N(N{:}CHPh)\end{array}>CPh,$$

formed in the first stage of the hydrolysis of 1 : 3-dibenzylideneamino-2-phenyl-2 : 3-naphthaglyoxaline or by prolonged boiling of the 1-amino-base with benzaldehyde in alcoholic solution, crystallises in slender, yellow or yellowish-brown needles and melts at 169°; the *hydrochloride*, $C_{24}H_{18}N_3Cl$, forms light yellow, slender needles and sinters at 210°, but does not melt at 285°; the *sulphate*, $C_{48}H_{36}O_4N_6S$, forms slender, yellow needles and sinters at 235°, but does not melt at 285°; the *picrate*, $C_{30}H_{20}O_7N_6$, forms slender, yellow needles and melts and decomposes at 248—249°. The *ethiodide*,



$$C_{10}H_6<\begin{array}{l}\text{——}N(EtI)\\ N(N{:}CHPh)\end{array}>CPh,$$

crystallises in slender, yellow needles and melts and decomposes at 218°.

1-o-*Nitrobenzylideneamino-2-phenyl-2 : 3-naphthaglyoxaline*,

$$C_{11}H_6N_2Ph\cdot N{:}CH\cdot C_6H_4\cdot NO_2,$$

crystallises in golden-brown needles and melts at 217—218°.

1-o-*Hydroxybenzylideneamino-2-phenyl-2 : 3-naphthaglyoxaline*,

$$C_{11}H_6N_2Ph\cdot N{:}CH\cdot C_6H_4\cdot OH,$$

crystallises in slightly yellow needles and melts and blackens at 284°.

2-*Phenyl-2 : 3-naphthaglyoxaline*,  $C_{10}H_6<\begin{array}{l}N\\ NH\end{array}>CPh$, is prepared together with benzylamine and dibenzylamine by reducing the 1-benzylideneamino-compound with zinc dust and glacial acetic acid; it crystallises in small needles or leaflets and melts at 210—211°, or, after resolidification, at 192°. The *hydrochloride*, $C_{17}H_{13}N_2Cl$, forms a yellow, crystalline mass and commences to sinter at 170°, but does not melt at 285°; the *sulphate*, $(C_{17}H_{12}N_2)_2,H_2SO_4$, is obtained as a yellow, flocculent precipitate. G. Y.

Conversion of Anthracene Derivatives into Azines and Dihydroazines. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co (D.R.-P. 167255).—When 1 : 3-dibromo-2-aminoanthraquinone is heated at 150° with nitrobenzene, copper chloride, and fused sodium acetate, a compound is produced which has the constitution of an *azine*,

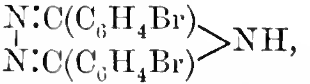
$$C_6H_4<\begin{array}{c}CO\\ CO\end{array}>C_6HBr<\begin{array}{c}N\\ |\\ N\end{array}>C_6HBr<\begin{array}{c}CO\\ CO\end{array}>C_6H_4.$$

At 180° an appreciable amount of the dihydroazine is also formed. The azine is obtained in the form of greenish-yellow, very sparingly soluble crystals which dissolve in fuming sulphuric acid and yield a colouring matter on boiling with aniline or quinoline (compare Abstr., 1905, i, 797). G. T. M.

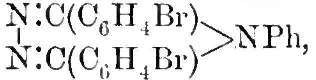
Conversion of Hydrazine Derivatives into Heterocyclic Compounds. XXI. Diacylhydrazide Dichlorides of Substituted Benzoic Acids and their Reaction Products. ROBERT STOLLÉ and ANTON WEINDEL (*J. pr. Chem.*, 1906, [ii], **74**, 1—12. Compare Stollé, this vol., i, 453; Stollé and Thoma, *ibid.*, 461).—*Di-*p-*bromobenzoylhydrazide dichloride*,

$$C_6H_4Br\cdot CCl{:}N\cdot N{:}CCl\cdot C_6H_4Br,$$

formed together with 2 : 5-di-*p*-bromophenyl-1 : 3 : 4-oxadiazole by heating di-*p*-bromobenzoylhydrazide with phosphorus pentachloride at 120°, separates from ether in stout, transparent crystals, from alcohol in transparent, slightly yellow leaflets, melts at 145°, dissolves in concentrated sulphuric acid, forming a golden-yellow solution, and yields 2 : 5-di-*p*-bromophenyl-1 : 3 : 4-oxadiazole when heated with alcoholic silver nitrate, or more slowly when boiled with water.

2 : 5-*Di*-p-*bromophenyl*-1 : 3 : 4-*triazole*,  $\left.\begin{array}{l}N{:}C(C_6H_4Br)\\ N{:}C(C_6H_4Br)\end{array}\right>NH$, formed by heating the dichloride with alcoholic ammonia in a sealed tube at 150°, crystallises in long needles, melts at 284°, dissolves in aqueous sodium hydroxide, and is reprecipitated by carbon dioxide, and forms a stable white *precipitate* with silver nitrate in alcoholic solution.

1-*Phenyl*-2 : 5-*di*-p-*bromophenyl*-1 : 3 : 4-*triazole*,



$$\left.\begin{array}{l}N{:}C(C_6H_4Br)\\ N{:}C(C_6H_4Br)\end{array}\right>NPh,$$

prepared by the action of aniline on the dichloride at 170°, crystallises in matted, slender needles and melts at 261°.

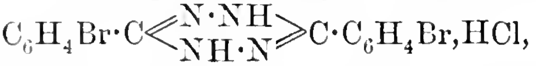
3 : 6-*Di*-p-*bromophenyl*-1 : 2-*dihydro*-1 : 2 : 4 : 5-*tetrazine*,

$$C_6H_4Br{\cdot}C\left<\begin{array}{c}N\text{——}N\\ NH{\cdot}NH\end{array}\right>C{\cdot}C_6H_4Br,$$

prepared by boiling the dichloride with hydrazine hydrate in ethereal solution, separates from benzene in yellow crystals, melts and decomposes at 235°, forming an intensely red liquid, and is oxidised by silver nitrate in alcoholic solution, metallic silver being precipitated, or more slowly on exposure of the alcoholic solution to air, forming 3 : 6-*di*-p-*bromophenyl*-1 : 2 : 4 : 5-*tetrazine*,

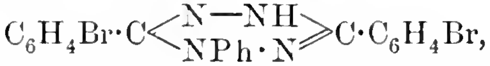
$$C_6H_4Br{\cdot}C\left<\begin{array}{c}N{\cdot}N\\ N{:}N\end{array}\right>C{\cdot}C_6H_4Br,$$

which crystallises from benzene in bluish-red leaflets and does not melt at 280°, but decomposes when more highly heated, yielding a colourless sublimate smelling of benzonitrile.

3 : 6-*Di*-p-*bromophenyl*-1 : 4-*dihydro*-1 : 2 : 4 : 5-*tetrazine hydrochloride*,  $C_6H_4Br{\cdot}C\left<\begin{array}{c}N{\cdot}NH\\ NH{\cdot}N\end{array}\right>C{\cdot}C_6H_4Br,HCl$, formed by the action of hydrogen chloride on the 1 : 2-dihydrotetrazine in alcoholic solution, crystallises in small prisms. The *base*, $C_{14}H_{10}N_4Br_2$, crystallises from alcohol in glistening, white needles, does not melt at 300°, and forms a stable, white *precipitate* with silver nitrate in alcoholic solution.

1 : 2-*Dibenzoyl*-3 : 6-*di*-p-*bromophenyl*-1 : 2-*dihydro*-1 : 2 : 4 : 5-*tetrazine*,  $C_6H_4Br{\cdot}C\left<\begin{array}{c}N\text{———}N\\ NBz{\cdot}NBz\end{array}\right>C{\cdot}C_6H_4Br$, prepared by the action of benzoyl chloride on the 1 : 2-dihydrotetrazine in pyridine solution, separates from alcohol as a yellow, crystalline powder and melts at 248°.

1-*Phenyl*-3 : 6-*di*-p-*bromophenyl*-1 : 4-*dihydro*-1 : 2 : 4 : 5-*tetrazine*,



$$C_6H_4Br{\cdot}C\left<\begin{array}{c}N\text{—}NH\\ NPh{\cdot}N\end{array}\right>C{\cdot}C_6H_4Br,$$

prepared by heating di-*p*-bromobenzoylhydrazide dichloride with phenylhydrazine in alcoholic solution on the water-bath, forms small, glistening, white, granular crystals and melts and decomposes at 260°.

The action of phenylhydrazine on di-p-bromobenzoylhydrazide dichloride in pyridine solution leads to the formation of 1-*phenyl*-3 : 6-*di*-p-*bromophenyl*-1 : 2-*dihydro*-1 : 2 : 4 : 5-*tetrazine*,

$$\mathrm{C_6H_4Br\cdot C}\begin{matrix}\diagup \mathrm{N}\text{———}\mathrm{N} \diagdown\\ \diagdown \mathrm{NPh\cdot NH} \diagup\end{matrix}\mathrm{C\cdot C_6H_4Br},$$

which crystallises from alcohol in yellow needles, melts and decomposes at 167°, and forms a brown *precipitate* with silver nitrate in alcoholic solution.

The action of m-nitrobenzylidenehydrazide and pyridine on di-p-bromobenzoylhydrazide dichloride in boiling benzene solution leads to the formation of 3 : 6-di-p-bromophenyl-1 : 2 : 4 : 5-tetrazine and 2 : 5-di-p-bromophenyl-1 : 3 : 4-oxadiazole.

Di-p-*bromobenzoylhydrazide diethyl ether*,

$$\mathrm{C_6H_4Br\cdot C(OEt){:}N\cdot N{:}C(OEt)\cdot C_6H_4Br},$$

formed by boiling the dichloride with sodium ethoxide in alcoholic solution in a reflux apparatus, crystallises in matted, slender needles, melts at 111°, and is hydrolysed by hydrochloric acid at 150°, forming hydrazine, p-bromobenzoic acid, and ethyl chloride. When heated with alcoholic ammonia in a sealed tube at 200°, it forms 2 : 5-di-p-bromophenyl-1 : 3 : 4-triazole.

Di-p-*chlorobenzoylhydrazide dichloride*,

$$\mathrm{C_6H_4Cl\cdot CCl{:}N\cdot N{:}CCl\cdot C_6H_4Cl},$$

forms large, glistening crystals, melts at 125°, dissolves in ether or hot alcohol, forming green solutions, and yields silver chloride only slowly when boiled with alcoholic silver nitrate.

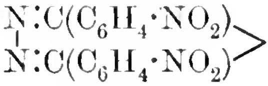
3 : 6-*Di*-p-*chlorophenyl*-1 : 2-*dihydro*-1 : 2 : 4 : 5-*tetrazine*, $C_{14}H_{10}N_4Cl_2$, forms yellow crystals, melts, becoming red, at 215°, and is oxidised to the *tetrazine*, which crystallises in bluish-red leaflets, by alcoholic silver nitrate at the ordinary temperature, by amyl nitrite in hot benzene solution, or more slowly on exposure of the alcoholic solution to air.

Di-p-*chlorobenzoylhydrazide dimethyl ether*,

$$\mathrm{C_6H_4Cl\cdot C(OMe){:}N\cdot N{:}C(OMe)\cdot C_6H_4Cl},$$

melts at 162°.

2 : 5-*Di*-o-*nitrophenyl*-1 : 3 : 4-*oxadiazole*,



$$\left.\begin{matrix}\mathrm{N{:}C(C_6H_4\cdot NO_2)}\\ |\\ \mathrm{N{:}C(C_6H_4\cdot NO_2)}\end{matrix}\right\rangle \mathrm{O},$$

crystallises in white needles and melts at 195°.

1-*Phenyl*-2 : 5-*di*-m-*nitrophenyl*-1 : 3 : 4-*triazole*, $C_{20}H_{13}O_4N_5$, crystallises in matted, white needles and melts at 215°.

The action of phosphorus pentachloride on benzoylhydrazide leads to the formation of 2 : 5-diphenyl-1 : 3 : 4-triazole and a *compound*, $\mathrm{NHBz\cdot NH\cdot P(N\cdot NHBz)_2}$, which crystallises from alcohol and melts at about 220°.

G. Y.

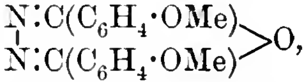
Conversion of Hydrazine Derivatives into Heterocyclic Compounds. XXII. Diacylhydrazide Dichlorides of Substituted Benzoic Acids and of α-Naphthoic Acid. Robert Stollé and Adolf Bambach (*J. pr. Chem.*, 1906, [ii], 74, 13—24. Compare Stollé, this vol., i, 453; Stollé and Thoma, *ibid.*, 461).—*Di*-p-*methoxybenzoylhydrazide*, $C_{16}H_{16}O_4N_2$, which forms colourless crystals and melts at 224°, is prepared together with *p*-methoxybenzoylhydrazide by the action of anisyl chloride on hydrazine sulphate in dilute potassium hydroxide solution. The latter substance is isolated as the *benzylidene* derivative, $C_{15}H_{14}O_2N_2$, which crystallises from alcohol in white needles and melts at 198°.

Di-p-*methoxybenzoylhydrazide dichloride*,

$$OMe{\cdot}C_6H_4{\cdot}CCl{:}N{\cdot}N{:}CCl{\cdot}C_6H_4{\cdot}OMe,$$

formed together with the corresponding oxadiazole, crystallises from ether or alcohol in needles or leaflets, melts at 130—150°, gives a golden-yellow coloration with concentrated sulphuric acid, and yields silver chloride when heated with alcoholic silver nitrate. In one preparation a *compound* containing chlorine and nitrogen, crystallising in green, glistening needles and melting at about 185°, and in another a white *chloro*-product melting at about 210°, were obtained.

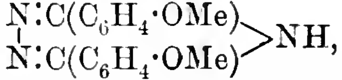
2 : 5-*Di*-p-*methoxyphenyl*-1 : 3 : 4-*oxadiazole*,



$$\left.\begin{matrix} N{:}C(C_6H_4{\cdot}OMe) \\ | \\ N{:}C(C_6H_4{\cdot}OMe) \end{matrix}\right>O,$$

formed by heating di-*p*-methoxybenzoylhydrazide with thionyl chloride in a reflux apparatus or alone at 260°, crystallises from alcohol in glistening, white needles, melts at 164°, and forms a white, flocculent *precipitate*, $C_{16}H_{14}O_3N_2,AgNO_3$, with silver nitrate in alcoholic solution, melting at 233°, and becoming violet on exposure to light.

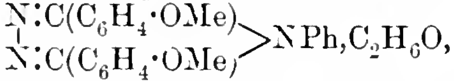
2 : 5-*Di*-p-*methoxyphenyl*-1 : 3 : 4-*triazole*,



$$\left.\begin{matrix} N{:}C(C_6H_4{\cdot}OMe) \\ | \\ N{:}C(C_6H_4{\cdot}OMe) \end{matrix}\right>NH,$$

forms white leaflets or rhombic crystals, melts when slowly heated at 180—182°, or at 150° if suddenly heated, dissolves in hot sodium carbonate solution, and yields a white *precipitate* with silver nitrate.

1-*Phenyl*-2 : 5-*di*-p-*methoxyphenyl*-1 : 3 : 4-*triazole*,



$$\left.\begin{matrix} N{:}C(C_6H_4{\cdot}OMe) \\ | \\ N{:}C(C_6H_4{\cdot}OMe) \end{matrix}\right>NPh,C_2H_6O,$$

crystallises in white, silky fibres, loses C_2H_6O at 100°, melts at 250°, is slightly soluble in acids, but insoluble in aqueous alkali hydroxides, and forms a flocculent precipitate with silver nitrate in alcoholic solution.

Di-p-*methoxybenzoylhydrazide diethyl ether*,

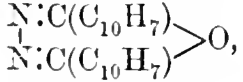
$$OMe{\cdot}C_6H_4{\cdot}C(OEt){:}N{\cdot}N{:}C(OEt){\cdot}C_6H_4{\cdot}OMe,$$

crystallises from alcohol in white needles, melts at 116—117°, and is hydrolysed by boiling hydrochloric acid and alcohol.

The action of phosphorus pentachloride on di-α-naphthoylhydrazide leads to the formation of *di-α-naphthoylhydrazide dichloride*,

$$C_{10}H_7{\cdot}CCl{:}N{\cdot}N{:}CCl{\cdot}C_{10}H_7,$$

which forms stout crystals, melts at 104—105°, gives an orange coloration with concentrated sulphuric acid, and is converted by silver nitrate in alcoholic solution into 2 : 5-*di-α-naphthyl*-1 : 3 : 4-*oxadiazole*,



$$\left.\begin{matrix} N{:}C(C_{10}H_7) \\ | \\ N{:}C(C_{10}H_7) \end{matrix}\right>O,$$

which forms a crystalline powder, melts at 175°, and shows a violet fluorescence in alcoholic or ethereal solution (compare Ekstrand, Abstr., 1887, 373, 840).

Di-p-*nitrobenzoylhydrazide dichloride*, $C_{14}H_8O_4N_4Cl_2$, crystallises from xylene or acetone in lemon-yellow needles, melts at 187°, and reacts with silver nitrate only slowly in boiling alcoholic solution.

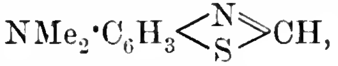
2 : 5-*Di*-p-*nitrophenyl*-1 : 3 : 4-*oxadiazole*, $C_{14}H_8O_5N_4$, crystallises in glistening, yellowish-brown or rose leaflets, melts at 302°, and is only sparingly soluble in hot organic solvents.

When heated with alcoholic ammonia at 200°, the dichloride yields 2 : 5-di-*p*-nitrophenyl-1 : 3 : 4-triazole (Pinner, Abstr., 1898, i, 94).

1-*Phenyl*-2 : 5-*di*-p-*nitrophenyl*-1 : 3 : 4-*triazole*, $C_{20}H_{13}O_4N_5$, separates from acetone in matted, white needles or from alcohol in small, stout crystals, melts at 270°, and forms a gelatinous *additive* compound with silver nitrate. G. Y.

Action of Formaldehyde on *as*-Dimethyl-*p*-phenylenediaminethiosulphonic Acid and a New Method of preparing Benzothiazoles. OTTO SCHMIDT (*Ber.*, 1906, **39**, 2406—2413. Compare Rügheimer, this vol., i, 418).—*Anhydroformaldehyde dimethyl*-p-*phenylenediamine mercaptan* [5-*dimethylamino*-2-*methyleneaminophenyl mercaptan*], $SH\cdot C_6H_3(NMe_2)\cdot N\colon CH_2$, is formed by the action of formaldehyde and hydrochloric acid on *as*-dimethyl-*p*-phenylenediaminethiosulphonic acid dissolved in aqueous ammonia; it polymerises rapidly and is isolated as the *ferrocyanide*,

$$3C_9H_{12}N_2S,2H_4Fe(CN)_6,5H_2O.$$

The action of sodium nitrite and hydrochloric acid on the freshly-prepared cooled solution of the mercaptan leads to the formation of 5-*dimethylaminobenzothiazole*,  $NMe_2\cdot C_6H_3<\substack{N\\S}>CH$, together with a small amount of a *substance*, which crystallises in matted, red needles and melts at 128°. The *benzothiazole* is formed also by boiling *as*-dimethyl-*p*-phenylenediaminethiosulphonic acid with formic acid; it crystallises in colourless leaflets, melts at 73—74°, is a feeble base, and gives a greenish-blue coloration, which becomes sky-blue on addition of water, with ferric chloride.

Sodium p-*dimethylaminomercaptoanilinomethylsulphite*,

$$SH\cdot C_6H_3(NMe_2)\cdot NH\cdot CH_2\cdot O\cdot SO_2Na,$$

is formed by heating the anhydro-compound with sodium hydrogen sulphite solution at 60°; it crystallises from concentrated sodium hydroxide solution, and when treated with sodium nitrite in dilute acetic acid solution yields 5-*dimethylamino*-1 : 2-*dihydrobenzothiazyl hydrogen sulphite*,  $NMe_2\cdot C_6H_3<\substack{NH\\S\text{—}}>CH\cdot O\cdot SO_2H$. This forms small, lemon-yellow leaflets or needles, does not melt at 300°, dissolves in strong acids or bases, forming coloured salts, and yields 5-dimethylaminobenzothiazole when heated or when boiled with aqueous alkali hydroxides. G. Y.

Compounds of Thiosulphuric Acid with Aldehydes. OTTO SCHMIDT (*Ber.*, 1906, **39**, 2413—2419. Compare preceding abstract; Vanino, Abstr., 1902, i, 744).—5-*Dimethylamino*-2-*methyleneaminophenylthiol formaldehydethiosulphate*,

$$[SH\cdot C_6H_3(NMe_2)\cdot N\colon CH_2,OH\cdot CH_2\cdot S_2O_3H]_3,$$

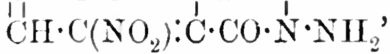
is formed by the action of sodium thiosulphate, formaldehyde, and hydrochloric acid on dimethyl-*p*-phenylenediaminethiosulphonic acid in ammoniacal solution; it crystallises in glistening, white, rhombic leaflets, melts and decomposes at about 122°, dissolves and partially decomposes when boiled with water, and is insoluble in organic solvents. When boiled with aqueous sodium hydroxide it forms sodium thiosulphate, formaldehyde, and the trimeride of the anhydro-mercaptan. In presence of an excess of formaldehyde, sodium thiosulphate is decomposed by hydrochloric acid, forming sulphuric acid, trithioformaldehyde being formed at the same time. If the formaldehyde is not in excess, sulphur and sulphur dioxide are formed. The decomposition of the formaldehydethiosulphate by hydrochloric acid takes place in the same manner.

The formaldehydethiosulphate is converted into 5-dimethylaminobenzothiazole in the same manner as is the free anhydro-compound (preceding abstract). G. Y.

Action of Carbonyl Chloride on 4-Acetylamino-*m*-phenylenediamine. Leopold Cassella & Co. (D.R.-P. 166680).—When carbonyl chloride is passed into a solution of 4-acetylamino-*m*-phenylenediamine in aqueous sodium carbonate, an insoluble carbamide is precipitated. This *diacetyltetra-aminodiphenylcarbamide* is insoluble in all the ordinary solvents and melts above 300°. When fused with sulphur at 240°, it yields a colouring matter containing sulphur, and soluble in alkali sulphides. G. T. M.

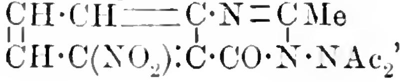
Colourless Soluble Salts of Rosaniline. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 163104).—Both triaminoditolylphenylcarbinol and triaminotritolylcarbinol dissolve in concentrated hydrochloric acid on a boiling water-bath, and crystals of a colourless salt separate on cooling. The product is washed with hydrochloric acid and dried in a vacuum, or, if necessary, washed with alcohol and ether. These salts dissolve very readily in cold water to form colourless solutions, which become red when heated, owing to dissociation. C. H. D.

Quinazolines. XV. A 3-Aminoquinazoline and the Corresponding 3:3′-Diquinazolyl from 6-Nitroacetylanthranil and Hydrazine Hydrate. Marston T. Bogert and Harvey A. Seil (*J. Amer. Chem. Soc.*, 1906, **28**, 884—893. Compare Abstr., 1905, i, 945).—When 6-nitroacetylanthranil (1 mol.) is added to hydrazine hydrate (1 mol.) in 33 per cent. aqueous solution, 5-*nitro*-3-*amino*-4-*keto*-2-*methyldihydroquinazoline*,



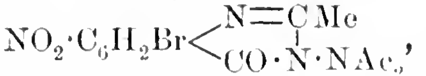
$$\begin{array}{l}\mathrm{CH\cdot CH{=\!=}C\cdot N{=}CMe}\\ \mathrm{CH\cdot C(NO_2){:}C\cdot CO\cdot N\cdot NH_2}\end{array}$$

is obtained; this crystallises in long, colourless prisms, melts at 152—153° (corr.), and is fairly soluble in water, alcohol, or acetone, slightly so in chloroform or benzene, and nearly insoluble in ether; the *hydrochloride* melts at 253—254° (corr.); the *platinichloride* forms yellow crystals. The *diacetyl* derivative,



$$\begin{array}{l}\mathrm{CH\cdot CH{=\!=}C\cdot N{=}CMe}\\ \mathrm{CH\cdot C(NO_2){:}C\cdot CO\cdot N\cdot NAc_2}\end{array}$$

crystallises from

warm alcohol in long, white, slender needles, melts at 233° (corr.), and yields a *bromo*-derivative,  $NO_2{\cdot}C_6H_2Br{<}\begin{matrix}N{=}CMe\\ CO{\cdot}N{\cdot}NAc_2\end{matrix}$, which separates from dilute alcohol in small, yellow crystals, softens at 105°, and melts at 110° (corr.).

The aminoquinazoline yields an *iso*nitrile-like odour with chloroform and potassium hydroxide, and undergoes condensation with benzaldehyde. It dissolves in warm aqueous potassium hydroxide to a purple-red solution, which, on neutralisation with acetic acid, deposits brown crystals of a nitrogenous *substance*, melting at 259—260° (uncorr.).

By the action of phenylhydrazine on the aminoquinazoline, 5-*nitro-3-phenylhydrazino-4-keto-2-methyldihydroquinazoline phenylhydrazone*,

$$\begin{matrix}CH{\cdot}CH{=\!=}C{\cdot}N{-\!-\!-\!-\!-\!-}CMe\\ CH{\cdot}C(NO_2){:}C{\cdot}C({:}N{\cdot}NHPh){\cdot}N{\cdot}NH{\cdot}NHPh\end{matrix}$$

is produced, which crystallises in large, white, lustrous plates and melts at 124—125° (corr.).

The aminoquinazoline does not react with potassium cyanate. 5-*Nitro-3-carbamino-4-keto-2-methyldihydroquinazoline*,

$$\begin{matrix}CH{\cdot}CH{=\!=}C{\cdot}N{=}CMe\\ CH{\cdot}C(NO_2){:}C{\cdot}CO{\cdot}N{\cdot}NH{\cdot}CO{\cdot}NH_2\end{matrix}$$

prepared by the condensation of 6-nitroacetylanthranil with semicarbazide, melts at 263—264° (uncorr.). The corresponding 7-*nitro*-compound, obtained from 4-nitroacetylanthranil and semicarbazide, forms masses of white, silky needles and melts at 266° (corr.); its aqueous solution gives a flocculent precipitate on the addition of bromine water; its *diacetyl* derivative melts at 229—230° (corr.).

5 : 5′-*Dinitro*-4 : 4′-*diketo*-2 : 2′-*dimethyltetrahydrodiquinazolyl*,

$$\begin{matrix}N{=}CMe\\ NO_2{\cdot}C_6H_3{\cdot}CO\end{matrix}{>}N{\cdot}N{<}\begin{matrix}CMe{:}N\\ CO{-}C_6H_3{\cdot}NO_2\end{matrix}$$

obtained by adding hydrazine hydrate (1 mol.) to finely-powdered 6-nitroacetylanthranil (2 mols.) so that the latter is always in excess, separates from a mixture of alcohol and acetone in small, granular crystals, melts at 306°, is not affected by acids or alkalis, and does not yield a bromo-derivative. The diquinazolyl can also be obtained, but only in very small yield, by condensing the aminoquinazoline with another molecule of 6-nitroacetylanthranil. The substance unites with 1 mol. of acetic anhydride to form an additive *compound* which crystallises in cubes, softens at 223°, and melts at 228° (corr.).

E. G.

Aminohydroxy-derivatives of the Phenylnaphthiminazoles.

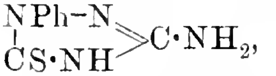
AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 167139).—When a nitrobenzaldehyde reacts with one of the naphthylene-*o*-diaminedisulphonic acids in the presence of acids, a nitrobenzylidene derivative is produced, which, when reduced, yields an aminophenylnaphthiminazoledisulphonic acid having the following formula:  $C_{10}H_4(SO_3H)_2{<}\begin{matrix}-N-\\ NH\end{matrix}{>}C{\cdot}C_6H_4{\cdot}NH_2$. On fusion with alkali hydroxides, the acid loses one of its sulpho-groups, and an aminohydroxy-derivative is produced.

3′-*Aminophenyl*-1 : 2-*naphthiminazole*-5 : 7-*disulphonic acid*, obtained by condensing *m*-nitrobenzaldehyde and naphthylene-1 : 2-diamine-5 : 7-disulphonic acid in sodium hydrogen sulphite solution and reducing the intermediate nitro-compound with iron filings and dilute hydrochloric acid, is a yellow powder moderately soluble in water and dissolving readily in aqueous alkalis; when fused with alkali hydroxides. it yields 3′-aminophenyl-5-hydroxy-1 : 2-naphthiminazole-7-sulphonic acid, an almost colourless powder, which is sparingly soluble in water, but readily dissolved by aqueous alkalis

Similar compounds are obtained from naphthylene-2 : 3-diamine-5 : 7-disulphonic acid, and the *m*-nitrobenzaldehyde may be replaced by other aldehydes, such as *p*-nitrobenzaldehyde and 3-nitro-4-dimethylaminobenzaldehyde-6-sulphonic acid. G. T. M.

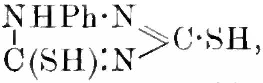
Action of Phenylhydrazine on Unsaturated Disulphides. Synthesis of Triazoles. EMIL FROMM and KURT SCHNEIDER (*Annalen*, 1906, **348**, 174—198).—The action of phenylhydrazine on perthiocyanic acid leads to the formation of phenyldithiourazole (3 : 5-dithiol-1-phenyl-1 : 2 : 4-triazole), 3-amino-5-thio-1-phenyl-4 : 5-dihydro-(or 5-amino-1-phenyl-3-thio-2 : 3-dihydro-)-1 : 2 : 4-triazole, and anilthiouret.

3-*Amino*-5-*thio*-1-*phenyl*-4 : 5-*dihydro*-1 : 2 : 4-*triazole*,



$$\begin{matrix}\text{NPh–N}\\ |\\ \text{CS·NH}\end{matrix}\!\!>\!\text{C·NH}_2,$$

crystallises from alcohol in slender, yellow needles, melts at 134·5°, is soluble in mineral acids or dilute alkali hydroxides or ammonia, and reacts with sodium hydroxide and benzyl chloride in alcohol, forming 3-*amino* 5-*thiobenzyl*-1-*phenyl*-1 : 2 : 4-*triazole*, $NH_2{\cdot}C_2N_3Ph{\cdot}SC_7H_7$, which crystallises in small needles, melts at 116·5°, is stable towards concentrated hydrochloric acid or fused potassium hydroxide, is oxidised by iodine, and evolves nitrogen with nitrous acid, but does not react with hydrogen sulphide in alcoholic ammoniacal solution. The *diacetyl* derivative, $C_{19}H_{18}ON_4S$, forms a white powder, melts at 122°, and is insoluble in acids or aqueous alkalis.

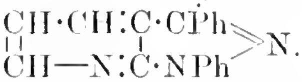
3 : 5-*Dithiol*-1-*phenyl*-1 : 2 : 4-*triazole*,  $\begin{matrix}\text{NHPh·N}\\ |\\ \text{C(SH):N}\end{matrix}\!\!>\!\text{C·SH}$, crystallises from glacial acetic acid in yellow needles, melts at 193°, is readily soluble in hot water or dilute alkali hydroxides or carbonates, has a strong acid reaction, gives precipitates with the salts of the heavy metals, and is stable towards boiling hydrochloric acid or lead oxide and sodium carbonate. The *acetyl* derivative crystallises in yellow needles and melts at 284—285°; the *dibenzyl ether*, $C_{22}H_{19}N_3S_2$, crystallises in stellate aggregates of needles and melts at 69·5°. When oxidised with iodine in alcoholic solution, the dithioltriazole yields the *product*, $C_{16}H_{10}N_6S_4$, which crystallises from glacial acetic acid and melts at 181°.

Anilthiouret,  $\text{NHPh·N:C}\!<\!\begin{matrix}\text{S·S}\\ \text{NH}\end{matrix}\!>\!\text{C:NH}$, crystallises from dilute hydrochloric acid as a yellow powder, melts at 224—227°, loses hydrogen sulphide when boiled with lead oxide and aqueous sodium carbonate, and when treated with benzyl chloride and sodium hydroxide is converted into *5-amino-3-thiobenzyl-1-phenyl-1 : 2 : 4-triazole*, $NH_2{\cdot}C_2N_3Ph{\cdot}S{\cdot}CH_2Ph$, which crystallises in thin, glistening leaflets, melts at 137°, and forms a *monoacetyl* derivative, $C_{15}H_{13}N_4SAc$; when condensed with acetone, anilthiouret yields the *product*, $C_8H_8N_4S_2$, which crystallises from alcohol and melts at 223°.

5-Amino-3-thiol- or *3-amino-5-thiol-1-phenyl-2-methyl-2 : 3-dihydro-1 : 2 : 4-triazole*, $C_9H_{10}N_4S$, formed by the action of *s*-phenylmethylhydrazine on perthiocyanic acid, crystallises in matted, white needles and melts at 213°. G. Y.

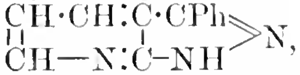
New Compound obtained by the Action of Iodine on Benzaldehyde Phenylhydrazone in Pyridine Solution.

Giovanni Ortoleva (*Gazzetta*, 1906, **36**, i, 473—476. Compare Abstr., 1904, i, 99).—The compound melting at 265—267°, to which the author previously ascribed the formula $C_{18}H_{18}N_3I$, is now shown to have the formula $C_{18}H_{14}N_3I$, and to be the hydriodide of a base, $C_{18}H_{13}N_3$, having the constitution



$$\begin{array}{l}\mathrm{CH{\cdot}CH{:}C{\cdot}CPh} \\ \mathrm{CH{-}N{:}C{\cdot}NPh}\end{array}\!\!>\mathrm{N}.$$

When treated with potassium permanganate, this compound gives a good yield of a new *base*,



$$\begin{array}{l}\mathrm{CH{\cdot}CH{:}C{\cdot}CPh} \\ \mathrm{CH{-}N{:}C{-}NH}\end{array}\!\!>\mathrm{N},$$

which crystallises from light petroleum in small, mammillary masses melting at 75—78° and is soluble in most organic solvents. This base yields a picrate and hydrochloride, and gives a white precipitate with silver nitrate or mercuric chloride. The *platinichloride* is red, and is decomposed by boiling water, giving the free base; when heated at 180—200°, it loses 4HCl and is transformed into the *platinosochloride*, $(C_{12}H_7N_3)_2PtCl_4$, which is obtained as a yellow powder. T. H. P.

Preparation of Substituted Di-iminobarbituric Acids.

Emanuel Merck (D.R.-P. 166448).—Malononitrile and its *C*-alkyl derivatives condense with carbamide and its homologues in the presence of the alkali metals or their amides or alkoxides to yield substituted di-iminobarbituric acids, which are readily converted into the corresponding barbituric acids; these products are of importance in therapeutics.

4 : 6-*Di-imino-2-oxy-5-diethylpyrimidine* was thus obtained from diethylmalononitrile, carbamide, and sodium ethoxide at 100°; it separates in crystalline aggregates and melts at 277° (corr.); it forms salts with the mineral acids, and is soluble in aqueous alkali hydroxides, but not in ammonia. G. T. M.

Soluble Double Salts of 1 : 3-Dimethylxanthine and 1 : 3 : 7-Trimethylxanthine with Barium Salicylate.

Aktien-Gesellschaft für Anilin-Fabrikation (D.R.-P. 168293).—When 1 mol. of barium salicylate and 2 mols. of 1 : 3-dimethylxanthine (theophylline) are mixed in warm water and the solution concentrated under diminished pressure, a soluble double salt is produced, which has the composition $Ba(C_7H_5O_3)_2,2C_7H_8O_2N_4$. A similar double salt,

$$Ba(C_7H_5O_3)_2,2C_8H_{10}O_2N_4,$$

is obtained from 1 : 3 : 7-trimethylxanthine. G. T. M.

Soluble Double Salts of 3 : 7-Dimethyl-1-ethylxanthine. J. D. Riedel (D.R.-P. 170302).—3 : 7-Dimethyl-1-ethylxanthine in aqueous solution combines with sodium benzoate or salicylate, and with lithium benzoate or salicylate to form soluble double salts, which are obtained either on evaporation or on adding alcohol or acetone. G. T. M.

[Colouring Matters of the Cyanine Series.] Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 167770).—2 : 6-*Dimethylquinoline*-p-*methoxyquinolinecyanine ethiodide* is produced by heating 2 : 6-dimethylquinoline ethiodide and *p*-methoxyquinoline ethiodide with alcoholic potash; it is precipitated by ether and recrystallised from alcohol, when it separates in lustrous, brown leaflets.

6 *Methoxy-2-methylquinoline-6-methylquinolinecyanine methiodide* is similarly obtained from the methiodides of 6-methoxy-2-methylquinoline and 6-methylquinoline by the action of potassium hydroxide in methyl-alcoholic solution; it separates in long, green needles. Both these cyanine colouring matters dissolve in alcohol to reddish-violet solutions. G. T. M.

Azoxy-compounds. Angelo Angeli and Guerriero Marchetti (*Atti R. Accad. Lincei*, 1906, [v], **15**, i, 480—482).—Treatment of a mixture of aniline and nitrobenzene with sodium yields a salt which ignites spontaneously in the air, the sodium content of which points to the formula $NPhNa\cdot NPhO\cdot ONa$; the salt is readily hydrolysed by water, yielding an appreciable proportion of azoxybenzene. Similarly, the condensation of α-naphthylamine with α-nitronaphthalene gives a compound from which a good yield of α-azoxynaphthalene is obtainable.

The interaction either of aniline and α-nitronaphthalene or of nitrobenzene and α-naphthylamine in presence of sodium yields two isomeric compounds, probably represented by the formulæ $NPh{:}NO\cdot C_{10}H_7$ and $NOPh{:}N\cdot C_{10}H_7$.

The condensation of the amines with nitro-derivatives in presence of sodium is hence general, the most important cases yet met with being represented by the following equations:

(1) $OH\cdot NH_2 + NO_2\cdot C_6H_5 = HO\cdot N_2O\cdot C_6H_5 + H_2O$.
(2) $OH\cdot NH_2 + NO_2\cdot OEt = HO\cdot N_2O\cdot OH + Et\cdot OH$.
(3) $C_6H_5\cdot NH_2 + NO_2\cdot OEt = C_6H_5\cdot N_2O\cdot OH + Et\cdot OH$.
(4) $C_6H_5\cdot NH_2 + NO_2\cdot C_6H_5 = C_6H_5\cdot N_2O\cdot C_6H_5 + H_2O$.

Each of the reactions (1) and (3) leads to the formation of isomeric products. T. H. P.

Decomposition of Azo-compounds by Sodium Hyposulphite. Eugène Grandmougin (*Ber.*, 1906, **39**, 2494—2497).—Sodium hyposulphite is a very convenient reducing agent for azo-compounds in boiling aqueous or alcoholic solutions. Azobenzene gives a quantitative yield of hydrazobenzene; α-nitroso-β-naphthol forms α-amino-β-naphthol-4-sulphonic acid (Böniger, Abstr., 1894, i, 199); Orange II, benzeneazo-β-naphthol, and benzeneazo-α-naphthol yield the corresponding aminonaphthols.

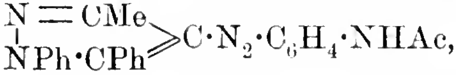
2-Amino-α-naphthol forms a *diacetyl* derivative which crystallises in white needles, melts at 116°, and by partial hydrolysis yields the *N*-acetyl compound, which has been previously described (compare Abstr., 1892, 861). C. S.

[Reduction of Nitroazo-compounds.] AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 169826).—5-Nitro-2-amino-*p*-tolyl methyl ether, $NO_2\cdot C_6H_2Me(OMe)\cdot NH_2$, when diazotised and combined with 7-amino-α-naphthol-3 : 6-disulphonic acid in alkaline solution, yields a nitroazo-derivative which, when gently warmed with aqueous sodium sulphide, yields an aminoazo-compound giving bluish-black shades on wool in an acid-bath. Other nitroazo-colouring matters are reduced under similar conditions. G. T. M.

Mixed Disazo-compounds from *p*-Phenylenediamine with Heterocyclic Side-chains. CARL BÜLOW and FRITZ BUSSE (*Ber.*, 1906, **39**, 2459—2466).—When benzoylacetone reacts in alcoholic solution with the diazonium compound obtained from acetyl-*p*-phenylenediamine, p-*acetylaminobenzene*-p-*azobenzoylacetone*,

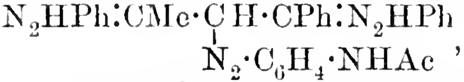
$$NHAc\cdot C_6H_4\cdot N_2\cdot CH(COPh)\cdot COMe,$$

is obtained. It separates from dilute alcohol in golden-yellow needles, melts at 171°, dissolves in dilute alkali to a dark red solution, and is reprecipitated unchanged by carbon dioxide. It reacts with phenylhydrazine in boiling glacial acetic acid to form two products which are separated mechanically. 4-p-*Acetylaminobenzeneazo*-1 : 5-*diphenyl-3-methylpyrazole*,



$\begin{array}{l} N = CMe \\ \vert \\ NPh\cdot CPh \end{array}\!\!>\!C\cdot N_2\cdot C_6H_4\cdot NHAc$,

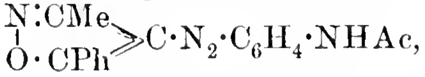
which forms orange-red crystals, melts and decomposes at 229° and is insoluble in dilute alkalis. The main product of the reaction is p-*acetylaminobenzeneazobenzoylacetone diphenylhydrazone*,



$$\begin{array}{l} N_2HPh{:}CMe\cdot CH\cdot CPh{:}N_2HPh \\ \qquad\qquad\quad \vert \\ \qquad\qquad\quad N_2\cdot C_6H_4\cdot NHAc \end{array},$$

which crystallises in yellow needles and melts at 206°.

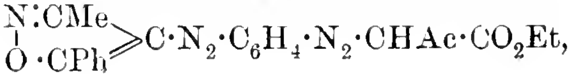
4-p-*Acetylaminobenzeneazo-5-phenyl-3-methyl*iso*oxazole*,



$$\begin{array}{l} N{:}CMe \\ \vert \\ O\cdot CPh \end{array}\!\!>\!C\cdot N_2\cdot C_6H_4\cdot NHAc,$$

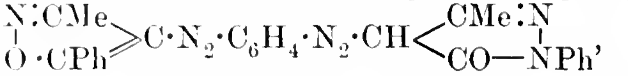
obtained from acetylaminobenzeneazobenzoylacetone and hydroxylamine in boiling alcoholic solution, separates from alcohol in large, yellow needles, melts and decomposes at 228°, and develops a red coloration with concentrated sulphuric acid. By hydrolysis with alcohol and 10 per cent. sodium hydroxide, 4-p-*aminobenzeneazo-5-phenyl-3-methyl*iso*oxazole*, $C_{16}H_{14}ON_4$, is obtained, which separates from alcohol in reddish-yellow, glistening needles and melts at 191°.

*Ethyl 5-phenyl-3-methyl*iso*oxazole-4-azobenzene*-p-*azoacetoacetate*,



$$\begin{array}{l} N{:}CMe \\ \vert \\ O\cdot CPh \end{array}\!\!>\!C\cdot N_2\cdot C_6H_4\cdot N_2\cdot CHAc\cdot CO_2Et,$$

obtained from an alcoholic solution of ethyl acetoacetate and the diazonium salt derived from the preceding compound, in the presence of sodium acetate, forms micro-crystalline, orange needles, melts at 151°, and dissolves in hot dilute alkalis with the loss of carbon dioxide.

*5-Phenyl-3-methyl*isoo*xazole-4-azobenzene*-p-*4'-azo-1'-phenyl-3'-methyl-5'-pyrazolone*,  $\begin{matrix}\text{N:CMe}\\ |\\ \text{O·CPh}\end{matrix}\!\!>\!\text{C·N}_2\text{·C}_6\text{H}_4\text{·N}_2\text{·CH}\!<\!\!\begin{matrix}\text{CMe:N}\\ \quad\ |\\ \text{CO—NPh}\end{matrix}$, is obtained when phenylhydrazine is slowly added to a glacial acetic acid solution of the preceding compound. It separates from its solution in nitrobenzene after the addition of alcohol or glacial acetic acid in red needles, melts and decomposes at 205—206°, dissolves in concentrated sulphuric acid to a reddish-violet solution, but is insoluble in hydrochloric acid or in a solution of sodium hydroxide.

The constitution of this compound has been confirmed by its formation in the reverse order by the following changes: 4-*p*-aminobenzeneazo-1-phenyl-3-methyl-5-pyrazolone (compare Abstr., 1900, i, 261) —> 1-*phenyl-3-methyl-5-pyrazolone-4-azobenzene*-p-*4'-azobenzoylacetone*, which melts and decomposes at 231—232°, —> 1-phenyl-3-methyl-5-pyrazolone-4-azobenzene-*p*-4'-azo-3'-phenyl-5'-methyl*iso*oxazole, which is identical with the compound previously described. C. S.

[The Diazotisation of Substituted Meta-diamines.] GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 168299).—2 : 4-Diaminophenol-6-carboxylic or -sulphonic acid can be readily diazotised to a bisdiazonium salt. Tolylene-2 : 4-diamine and 4-chloro-*m*-phenylenediamine, on the other hand, do not diazotise readily, for the diazonium salt first formed combines with the still undiazotised diamine to form azo-compounds of the type of Bismarck brown. 2 : 4-Diaminophenol, which might also be expected to yield azo-derivatives by this secondary reaction, is found, however, to diazotise quite readily in the presence of sufficient mineral acid. The solution of the bisdiazonium salt has a reddish-yellow colour, and the compound combines with the *α*-naphtholsulphonic acids (5 and 6), even in acetic acid solutions, to yield an intermediate azodiazo-product, which in alkaline solutions condenses further with a phenol or phenolsulphonic acid to give rise to a tetrazo-colouring matter. G. T. M.

Occurrence of Glycyl-proline Anhydride in the Tryptic Decomposition Products of Gelatin. PHOEBUS A. LEVENE and WALLACE A. BEATTY (*Ber.*, 1906, 39, 2060—2061).—The compound $C_7H_{10}O_2N_2$, described previously (this vol., i, 469), is readily hydrolysed when heated at 150° with concentrated hydrochloric acid. The products obtained are *α*-proline [pyrrolidine-2-carboxylic acid] and glycine, and the original substance thus appears to be glycyl-proline anhydride. J. J. S.

Formation of Dipeptides by the Hydrolysis of Proteids. EMIL FISCHER and EMIL ABDERHALDEN (*Ber.*, 1906, 39, 2315—2320. Compare this vol., i, 326; Levene and Beatty, preceding abstract).—Detailed instructions are given for the isolation of *glycyl*-l-*tyrosine* *anhydride*, $C_{11}H_{12}O_3N_2$, from the products of the hydrolysis of silk-fibroin by hydrochloric acid. It separates from hot water in a felted mass of colourless needles, melts and decomposes at 278—283° (corr.), is hydrolysed by 25 per cent. sulphuric acid to tyrosine and glycine, and is identical with the synthetic product in crystalline form, melting point, and solubility, but differs slightly in rotatory power, $[\alpha]_D$ at 20° being 123·3° as against 126·4°.

Glycyl-l-*leucine anhydride*, $C_8H_{11}O_2N_2$, has been isolated from the products of hydrolysis of elastin by 70 per cent. sulphuric acid; it separates slowly from hot alcohol or acetone in microscopic needles, melts at 253° (corr.), has $[\alpha]_D$ 29·2° at 20°, is hydrolysed by concentrated hydrochloric acid at 100° to glycine and leucine, and is identical with the synthetically prepared anhydride. C. S.

The True Nature of the "Leucines" and "Glucoproteins" obtained by Schützenberger in the Decomposition of Proteid Matter. LOUIS HUGOUNENQ and ALBERT MOREL (*Compt. rend.*, 1906, **142**, 1426—1428).—By fractional precipitation by means of phosphotungstic acid, Schützenberger's leucines, "leuceines," and "glucoproteins" (Abstr., 1877, i, 725; 1879, 542) can be separated into well-known amino-acids; thus, the leucine group $C_nH_{2n+1}O_2N$ contains 10 per cent. of alanine, 41 per cent. of leucine, 2·8 per cent. of phenylalanine, 1 per cent. of aspartic acid, 0·8 per cent. of glutamic acid, and 5 per cent. of tyrosine; the leucine group $C_nH_{2n-1}O_2N$ contains 0·27 per cent. of tyrosine, 21 per cent. of alanine, 31 per cent. of leucine, 5·8 per cent. of proline, 19 per cent. of phenylalanine, 3·9 per cent. of aspartic acid, and 1·9 per cent. of glutamic acid; and the gluocoprotein group, $C_nH_{2n}O_4N$, contains 13 per cent. of alanine, 12 per cent. of leucine, 0·2 per cent. of proline, 7 per cent. of phenylalanine, 5 per cent. of aspartic acid, and 12 per cent. of glutamic acid. M. A. W.

The "Chlorination" of Wool. LÉO VIGNON and J. MOLLARD (*Compt. rend.*, 1906, **142**, 1343—1345).—The authors have examined the action of gaseous chlorine, chlorine water, and bleaching powder, in acid solution on wool, and find that whilst it is dissolved by the prolonged action of the gas, its properties are modified when the action is limited, and it loses 10 per cent. of its weight, is dyed more readily, giving deeper and more brilliant tints, and becomes unshrinkable. The chlorine is not fixed by the wool, but it appears to destroy the projecting points (hooks) of the scales, and thus diminish its aptitude for felting and shrinking; at the same time the increase in the acid and basic functions caused by the rupture of certain linkings of amino-acids would account for the increase in the tinctorial properties.

M. A. W.

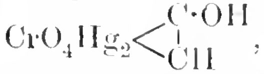
Compounds of Nucleic Acid and Proteid, with Special Reference to those in the Mammary Gland and their Relation to Caseinogen Formation. WILHELM LÖBISCH (*Beitr. chem. Physiol. Path.*, 1906, **8**, 191—209).—Nucleic acid from the mammary gland in its composition and properties is closely related to the nucleic acids from the thymus and spermatozoa, and not to guanylic acid. It yields a carbohydrate group. The hypothesis that caseinogen is a simple compound of this acid with the serum proteid is not tenable. The reason for this view and the general theoretical conceptions of the way in which nucleic acid can unite with proteids are discussed. W. D. H.

Crystalline Chitosan Compounds from Sepia Shells. OTTO VON FÜRTH and MICHELE RUSSO (*Beitr. chem. Physiol. Path.*, 1906, **8**, 163—190).—Chitosan hydrochloride and hydrobromide can be obtained in characteristic crystalline form. Araki's formula, $C_{14}H_{26}O_{10}N_2$, for chitosan is disputed; the molecule is at least twice, perhaps four times, heavier. It contains neither aldehyde nor carboxyl groups, and its nitrogen has the character of a secondary amine. It can combine with one molecule of hydrochloric acid for each atom of nitrogen; the compound is a loose one, and some of the acid is removable in a vacuum. On decomposition with acids, the hydrochloride yields acetic acid 25 and glucosamine 60 per cent. All the glucosamine complexes appear to be acetylated. It takes up one benzoyl group per nitrogen atom. A large part of the oxygen in the molecule is present in hydroxylic form. Chitosan gives with bromine a scarlet additive product from which the bromine is removed by warming with water. The chitosans obtained from the skeletal substance of arthropods and molluscs are identical. The integuments of butterfly pupæ are made of chitin, not of Griffiths' pupin. W. D. H.

Action of Light on Enzymes in Oxygen and in Hydrogen, compared with the Action of Photodynamic Substances. A. JODLBAUER and HERMANN VON TAPPEINER (*Chem. Centr.*, 1906, i, 487; from *Arch. Klin. Med.*, **85**, 386—394).—Fluorescent substances, even with intense light, only act in presence of oxygen. Sunlight, deprived of ultra-violet rays, will alone injure invertin when oxygen is present. It is probable that photodynamic action consists in a quickening of the simple action of light. This quickening action is very considerable. The effect of sunlight and eosin in concentrations of $N/2000$ (optimum) in ten minutes was four times as great as that of sunlight, free from ultra-violet rays, in fifteen minutes. N. H. J. M.

The Supposed Identity of Pepsin and Rennin. SIGVAL SCHMIDT-NIELSEN (*Zeit. physiol. Chem.*, 1906, **48**, 92—109).—The conclusion is drawn that the enzyme which curdles neutral milk cannot be identical with pepsin. W. D. H.

Organic Chemistry.

Reactions of Acetylene with Acidified Solutions of Mercury and Silver Salts. JULIUS A. NIEUWLAND and J. A. MAGUIRE (*J. Amer. Chem. Soc.*, 1906, 28, 1025—1031. Compare Nieuwland, Abstr., 1905, i, 557; Poleck and Thummel, Abstr., 1890, 118; Hofmann, Abstr., 1905, i, 268).—When passed into a solution of mercuric chromate in aqueous chromic acid, acetylene forms a bright yellow *precipitate*,  $\mathrm{CrO_4Hg_2}<\begin{array}{l}\mathrm{C{\cdot}OH}\\ \;|\\ \mathrm{CH}\end{array}$, which becomes brown when dried, forms iodoform with moist iodine, especially in alkaline solution, deflagrates, forming carbon and chromium oxide, when rubbed in a mortar or touched with a hot glass rod, and dissolves in presence of nascent chlorine. With mercuric silicofluoride, acetylene forms a white precipitate which turns blue, has an odour of aldehyde, decomposes even when dry, gives the iodoform reaction, reacts energetically with dry bromine or chlorine, and is decomposed by concentrated hydrochloric acid. A similar *precipitate* is formed by the action of acetylene on mercuric fluoroborate.

The white *precipitate* obtained on passing acetylene into a solution of mercuric chlorate in chloric acid is extremely explosive when rubbed, on percussion, or on contact with sulphuric acid, yields acetaldehyde in contact with water, and gives the iodoform reaction in alkaline solution; it decomposes only slowly when moist, attacks organic matter such as paper, and is soluble in acids. A similar *precipitate* is formed with mercuric perchlorate; when pure this is not exploded by heat, friction, or treatment with sulphuric acid. Acetylene and mercuric nitrite interact with development of heat, forming a heavy, cream-coloured *precipitate*, $C_2(HgNO_2)_2$, which decomposes when heated and gives the iodoform reaction in alkaline solution. Similar white *precipitates* are formed by acetylene with mercury acetamide and mercuric bromate.

Acetylene forms explosive *precipitates* with silver fluoride, nitrite, silicofluoride, fluoroborate, and bromate in acid solutions and with silver chloride in sodium hyposulphite solution. The *precipitate*, $3C_2H_2,2H_3PO_4,Ag_3PO_4,H_2O$, formed from acetylene and silver phosphate in acid solution, is stable, swells and decomposes when heated, is only slowly decomposed when acted on by light, and dissolves in potassium cyanide solution, liberating acetylene. Acetylene does not form precipitates with silver chromate or cyanide, but with silver perchlorate it yields an extremely explosive *compound* which is dangerous to prepare even in the smallest quantity. These compounds of silver and acetylene do not give the iodoform reaction, and with the exception of the phosphate are rapidly blackened on exposure to light.

G. Y.

Derivatives of $\alpha\gamma\epsilon$-Hexatriene. PIETER VAN ROMBURGH and W. VAN DORSSEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, **9**, 111—115. Compare this vol., i, 130, 141).—A new preparation of the hydrocarbon, $CH_2:CH\cdot CH:CH\cdot CH:CH_2$ (by heating the formate of *s*-divinyl glycol), which was purified by fractionation from sodium and finally distilling in an atmosphere of carbon dioxide, boiled at 77—78·5° under a pressure of 764·4 mm.; it had a sp. gr. 0·749 and n_D 1·4884 at 13·5°.

When treated with bromine at −10°, the dibromide, $C_6H_8Br_2$, is obtained as colourless crystals melting at 85·5—86°; at higher temperatures a tetrabromide, $C_6H_8Br_4$, is obtained, melting at 114—115°; at the same time a *hexabromide*, $C_6H_8Br_6$, is always produced, and can be separated by ethyl acetate, and melts at 163·5—164°. The dibromide and tetrabromide are identical with compounds obtained by Griner by the action of phosphorus tribromide on *s*-divinyl glycol. These facts show that the dibromide has the constitution

$$CH_2:CH\cdot CHBr\cdot CHBr\cdot CH:CH_2,$$

and that the addition of the bromine to the hexadiene has not followed Thiele's rule.

When reduced with hydrogen at 125—130° in the presence of nickel, *n*-hexane is formed. When the hexatriene is reduced with sodium and alcohol, a mixture of hexene and a hexadiene is obtained which could not be resolved into its constituents. It is suggested that the reduction has followed two courses: first a mixture of two hexadienes, the $\beta\delta$, $CHMe:CH\cdot CH:CHMe$, and the $\beta\epsilon$, $CHMe:CH\cdot CH_2\cdot CH:CH_2$, is produced; the former alone can be further reduced by this method, yielding γ-hexene, $CH_2Me\cdot CH:CH\cdot CH_2Me$. K. J. P. O.

Reduction of Unsaturated Primary Alcohols of the Fatty Series by Metal-ammonium Compounds. E. CHABLAY (*Compt. rend.*, 1906, **143**, 123—126. Compare Abstr., 1905, i, 502).—The unsaturated primary alcohols of the fatty series react with metal-ammonium compounds to form the corresponding unsaturated hydrocarbon according to the equation

$$2C_nH_{2n-1}OH + 2NH_3Na = C_nH_{2n-1}ONa + NaOH + C_nH_{2n} + 2NH_3.$$

From allyl alcohol, propylene is thus obtained in quantitative yield. The reaction is extremely energetic and is best conducted by allowing the alcohol to fall drop by drop into the solution of the metal-ammonium compound at −40°. The reaction has also been tried with citronellol, which yields a hydrocarbon boiling at 168—169° under 760 mm. pressure. It has a sp. gr. 0·789 at 0°, 0·777 at 22·5°, $n_D = 1{\cdot}4484$ at 22·6°. It is probably $CMe_2:CH\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH_2\cdot CH_3$, but a small quantity only has been obtained.

It is to be noted that sodium gives both hydrogen and propylene with allyl alcohol, whereas sodammonium yields only the hydrocarbon.

H. M. D.

Determination of the Molecular Weights of Alcohols and of Phenols by the Use of Benzoic Anhydride. ALBERT GASCARD (*J. Pharm. Chim.*, 1906, [vi], **24**, 97—101).—When an alcohol or phenol is esterified by means of benzoic anhydride, one molecule of benzoic acid is formed for each molecule of alcohol or phenol originally taken, according to the equation $R\cdot OH+(COPh)_2O=Ph\cdot CO_2R+Ph\cdot CO_2H$, and the molecular weight of the alcohol or phenol can therefore be determined by estimating the benzoic acid present in the resulting mixture. The method of procedure is as follows: about half a gram of the pure alcohol or phenol is placed in a long-necked flask together with two or three times the calculated quantity of benzoic anhydride, the flask is sealed and heated for about twenty-four hours by complete immersion in a bath of water, saturated solution of calcium chloride, or oil, according to the temperature required to complete the esterification; the flask is cooled and opened, and 10 to 20 c.c. pure ether, benzene, or chloroform added to dissolve the mixture of ester, anhydride, and acid; 5 c.c. of water are then added and the acid titrated by means of normal potassium carbonate in the presence of phenolphthalein; the molecular weight (P) of the alcohol is given by the equation $P=p\times 1000/N$, where p is the weight of alcohol taken and N is the number of c.c. of alkali employed. As benzoic anhydride usually contains a little free benzoic acid it is advisable to make a blank experiment to determine the amount; but control experiments show that neither benzoic anhydride nor the ester of a primary or secondary alcohol is appreciably hydrolysed under the conditions of the experiment. M. A. W.

Boiling Points of some Secondary and Tertiary Alcohols. GUSTAV D. HINRICHS (*Compt. rend.*, 1906, **143**, 359—361).—The author has previously shown (this Journal, 1873, 1014) that the boiling point of a compound is a function of its maximum moment of inertia; the secondary and tertiary alcohols, $C_nH_{2n+1}OH$, examined by Henry (following abstract), afford a further illustration of this generalisation; their maximum moments of inertia are given below, and the order is the same as that observed by Henry in their boiling points.

For *n*.	5.	6.	7.	8.	9.
Tertiary alcohol.........	79	168	309	501	746
Secondary alcohol	82	161	286	468	712

M. A. W.

Secondary Alcohols from the Octane, $CHMe_2\cdot[CH_2]_4\cdot CH_3$. LOUIS HENRY [with BUELENS and MUSET] (*Compt. rend.*, 1906, **143**, 102—104).—Whilst the secondary alcohols derived from normal octane have approximately the same boiling point, it is found that the boiling points of the various secondary alcohols derived from the β-methyloctane, $CHMe_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_3$, differ considerably. The boiling rises regularly as the distance of the carbinol group from the carbon atom to which the two methyl groups are attached increases. The respective boiling points are γ 153—154°, δ 160—161°, ε 165—166°, ζ 171—172°.

When the γ-alcohol is converted into the corresponding halogen compound and this is hydrolysed, the tertiary dimethylpentylcarbinol,

$C_5H_{11}\cdot CMe_2\cdot OH$, is obtained, and this boils at 162°, which is considerably higher than the boiling point of the secondary γ-alcohol. If the boiling points of the secondary alcohols,

$$CHMe_2\cdot CH(OH)\cdot C_nH_{2n+1},$$

are compared with those of the tertiary alcohols,

$$OH\cdot CMe_2\cdot CH_2\cdot C_nH_{2n+1},$$

it is found that the relationship between the boiling points changes as the number of carbon atoms in the molecule increases. In the case of pentane and hexane the secondary alcohol boils 10° and 6° respectively above the tertiary alcohol; the alcohols derived from heptane have the same boiling point, whilst in the case of octane the tertiary alcohol boils 8° higher than the corresponding secondary compound.

H. M. D.

Transformation of Secondary-tertiary α-Glycols into Ketones and the Transposition of Hydrobenzoin.

Marc Tiffeneau and Dorlencourt (*Compt. rend.*, 1906, **143**, 126—128).—γ-Ethylpentylene βγ-glycol, obtained by the action of magnesium ethyl bromide on ethyl lactate, boils at 194—197° under the ordinary pressure and has a sp. gr. 0·957 at 20°. When heated with sulphuric acid it yields diethylacetone. *αα-Diphenylpropylene αβ-glycol* melts at 96°, and in the same way yields diphenylacetone melting at 45—47°, which gives a *semicarbazone* of melting point 165—166°.

α-Phenyl-β-ethylbutylene αβ-glycol, which melts at 89°, is converted by sulphuric acid into phenyl *iso*pentyl ketone, $C_6H_5\cdot CO\cdot CHEt_2$. This boils at 230—236° and yields a semicarbazone melting at 179°.

Methylhydrobenzoin, melting at 104°, is converted into methyl deoxybenzoin, which boils at 193° under 25 mm. pressure and gives a semicarbazone melting at 194°.

In the same way ethylhydrobenzoin, melting at 117°, yields ethyldeoxybenzoin, the semicarbazone of which melts at 167°.

These changes are quite analogous to the formation of diethylacetone and diphenylacetone from ethylpentylene glycol and diphenylpropylene glycol respectively, and the intramolecular transposition which takes place in the formation of diphenylacetaldehyde from hydrobenzoin is quite exceptional. The phenomenon of dehydration in the case of glycols of the type $ArCH(OH)\cdot CH(OH)Ar'$ is therefore different from that of glycols of the general formula $ArRC(OH)\cdot CH(OH)Ar'$.

H. M. D.

Rectification of Officinal Ethyl Ether.

P. Guigues (*J. Pharm. Chim*, 1906, [vi], **24**, 204).—Ethyl ether containing alcohol can be conveniently purified by distillation over colophony, which retains the alcohol. Five per cent. of 98 per cent. alcohol was added to pure anhydrous ether having a sp. gr. 0·720 at 15°, the sp. gr. of the mixture after drying over anhydrous potassium carbonate was 0·725, and this fell to 0·721 after once washing with water; the ether, still retaining 1 per cent. of alcohol, was placed in contact with colophony (50 grams per litre of ether), and finally distilled; the distillate was pure ethyl ether having a sp. gr. 0·720 at 15°.

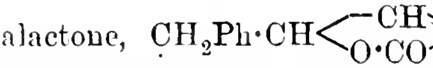
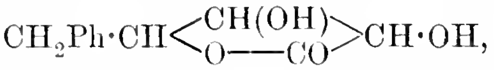
M. A. W.

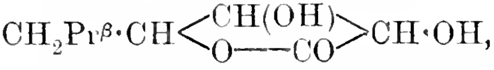
Triformin (Glyceryl Triformate). PIETER VAN ROMBURGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, 9, 109—111).—Although diformin is produced as an intermediate product in the preparation of formic acid from oxalic acid and glycerol, it is difficult to demonstrate the presence of triformin. When a large excess of anhydrous oxalic acid is used and the product distilled under reduced pressure, an oil is obtained which has a sp. gr. 1·309 at 25°, and by titration is shown to consist of 90 per cent. of triformin. Similar results are obtained when pure diformin is treated with anhydrous formic acid. The triformin may be isolated from these mixtures by cooling the oil with liquid ammonia, when crystals separate, which can be freed from liquid. Triformin crystallises in needles melting at 18°, and as a liquid has a sp. gr. 1·320 and n_D 1·4412 at 18°; it boils at 163° under 38 mm. and at 266° under the ordinary pressure. If mixed with diformin, distillation at the ordinary pressure is accompanied by decomposition, carbon monoxide and dioxide being evolved and allyl formate distilling over. On very slow distillation at the ordinary pressure, triformin decomposes into allyl formate, formic acid, and allyl alcohol, which distil, and glycerol which remains in the residue, the oxides of carbon being at the same time evolved.

Triformin is hydrolysed slowly by cold water, but more rapidly by warm water. It reacts with ammonia and amines, yielding the corresponding formamide and glycerol. K. J. P. O.

The Fatty Acids of Kephalin. H. COUSIN (*J. Pharm. Chim.*, 1906, [vi], 24, 101—108. Compare Koch, this vol., ii, 136).—Kephalin, precipitated by alcohol from an ethereal extract of dried ox's brain and purified by repeated treatment with boiling alcohol, forms a firm, waxy, pale yellow mass, becoming reddish-brown with time; it is insoluble in water or acetone, slightly soluble in ethyl acetate or cold alcohol, soluble in hot alcohol; it contains from 3·73 to 3·89 per cent. of phosphorus and 1·82 to 1·86 per cent. of nitrogen, which correspond with the ratios P : N = 2·0 to 2·12. The nitrogen bases were removed by partial hydrolysis by heating with a dilute hydrochloric acid, and the residual mixture of fatty acids and glycerophosphoric esters completely saponified by prolonged boiling with an alcoholic solution of potassium hydroxide in alcohol. The glycerophosphoric acid was isolated in the form of its calcium salt, and the mixture of fatty acids, having an iodine value 96 to 102, was separated according to the method previously employed in the case of lecithin (Abstr., 1903, i, 675; this vol., i, 330) into unsaturated and saturated acids. The unsaturated acid or acids (Thudichum's "kephalic acid") is either linoleic acid or a mixture of acids belonging to this series, and stearic acid is the only saturated acid. M. A. W.

Constitution of Phenylangelicalactone and *iso*Octenelactone. JOHANNES THIELE and WILHELM WEDEMANN (*Annalen*, 1906, 347, 132—142).—It has been shown by Fittig that both the Δ^1 and Δ^2 crotonolactones yield the same γ-ketonic acid. Two such lactones, phenylangelicalactone and *iso*octenelactone, have been here demonstrated to have the Δ^1 constitution.

When phenylangelicalactone,  $CH_2Ph\cdot CH{<}\genfrac{}{}{0pt}{}{-CH}{O\cdot CO}{>}CH$, is oxidised with permanganate in neutral alcoholic solution, *phenyldihydroxyvalerolactone*,  $CH_2Ph\cdot CH{<}\genfrac{}{}{0pt}{}{CH(OH)}{O\text{——}CO}{>}CH\cdot OH$, is obtained, crystallising in needles melting at 124°. With acetyl chloride, it yields a *diacetyl* derivative, $C_{15}H_{16}O_6$, as a thick oil, and with *p*-nitrobenzoyl chloride, a p-*nitrobenzoate*, $C_{25}H_{18}O_{10}N_2$, which crystallises in needles melting at 130°. On hydrolysis with barium hydroxide, the barium salt of trihydroxyphenylvaleric acid is formed; the *silver* salt is an amorphous precipitate.

*iso*Octenelactone,  $CH_2Pr^{\beta}\cdot CH{<}\genfrac{}{}{0pt}{}{-CH}{O\cdot CO}{>}CH$, is prepared by the action of anhydrous sodium acetate on $\beta\gamma$-dibromo*iso*octenoic acid, and is an oil of pleasant odour. When oxidised, it yields *αβ-dihydroxy-γ-iso-butylbutyrolactone*,  $CH_2Pr^{\beta}\cdot CH{<}\genfrac{}{}{0pt}{}{CH(OH)}{O\text{——}CO}{>}CH\cdot OH$, which crystallises in needles melting at 124°. The *di*-p-*nitrobenzoate*, $C_{22}H_{20}O_{10}N_2$, melts at 147°. On hydrolysis, it yields αβγ-trihydroxy-γ-*iso*butylbutyric acid, the *silver* salt of which was analysed. K. J. P. O.

Reactions between Acid Chlorides and Potassium Ethylxanthate.

Oswin W. Willcox (*J. Amer. Chem. Soc.*, 1906, **28**, 1031—1034).—The action of acetyl chloride on potassium ethylxanthate in cooled dilute ethereal solution leads to the formation of the mixed *anhydride*, OEt·CS·SAc, which is obtained as an unstable oil, decomposing when heated into ethyl acetate, carbon disulphide, and other products. In presence of a small amount of ether and without cooling, the action leads to the formation of ethylxanthic anhydride. Only a small amount of this could be obtained from the product of the action of ethyl chlorocarbonate on potassium ethylxanthate.

Ethyl pentathiotricarbonate, $CS(S\cdot CS\cdot OEt)_2$, is formed by the action of thiocarbonyl chloride on potassium ethylxanthate in ice-cooled aqueous solution, or together with a yellowish-brown oil in acetone solution; it separates from benzene in white, microscopic crystals, melts and decomposes at 160°, and is stable towards dilute acids or alkali hydroxides, but is decomposed, depositing sulphur, when heated with concentrated sulphuric acid.

Large amounts of ethylxanthic anhydride are isolated from the product of the action of carbonyl chloride on potassium ethylxanthate in toluene solution. G. Y.

*iso*Succinic Acid.

Richard Meyer and Paul Bock (*Annalen*, 1906, **347**, 93—105).—The preparation of ethyl *iso*succinate from ethyl γ-bromopropionate and potassium cyanide is unsatisfactory. Attempts to employ Grignard's reaction by treating ethyl γ-bromopropionate successively with magnesium and carbon dioxide were unsuccessful. It was found that the purification of the product of the malonic ester synthesis by conversion of the impure ethyl *iso*succinate into the crystallisable amide afforded the best results.

Benzyl iso*succinate* is an oil; the p-*nitrobenzyl* ester, prepared from impure silver *iso*succinate and *p*-nitrobenzyl iodide, crystallises in six-sided plates melting at 75°, but cannot be readily converted into *iso*succinic acid. The *anilide* of *iso*succinic acid is obtained by heating the ester with aniline, and crystallises in needles melting at 180—181°.

*iso*Succinamide is easily hydrolysed by boiling with dilute aqueous sodium hydroxide. The acid, which crystallises in white needles, melts at 127—130° and forms a 50·61—50·87 per cent. solution in water at 15°. Its molecular heat of combustion was found to be 365·3 Cal. (constant volume), a number in near agreement with Stohmann's value.

Cadmium *iso*succinate crystallises with H_2O in sparingly soluble needles. The *cupro-ammonium* compound,

$$Cu(CO_2\cdot C_2H_4\cdot CO_2NH_4)_2,4H_2O,$$

prepared from ammonium *iso*succinate and copper acetate, forms bluish-green crystals. *iso*Succinyl chloride, prepared from thionyl chloride and *iso*succinic acid or, better, sodium *iso*succinate, is a liquid boiling at 75° under 50 mm. pressure. Bromo*iso*succinic acid, prepared from the pure *iso*succinic acid, forms large, transparent crystals, apparently octohedral, and melts and decomposes at 165—170°.

K. J. P. O.

Esterification of Unsymmetrical Di- and Poly-basic Acids. XIV. *i*-Aspartic Acid.

Rudolf Wegscheider and Erich Frankl (*Monatsh.*, 1906, **27**, 487—501. Compare Wegscheider, this vol., ii, 77).—As stated by Piutti (Abstr., 1888, 677; 1889, 383), the esterification of *i*-aspartic acid by means of alcohol and hydrogen chloride leads to the formation of *β*-ethyl hydrogen *i*-aspartate, together with traces of the diethyl ester (compare Curtius and Koch, Abstr., 1885, 885; Fischer, Abstr., 1901, i, 192).

The action of silver nitrate on ammonium *i*-aspartate in aqueous solution leads to the formation of the *salt*, $C_4H_6O_7N_2Ag_2$. A salt of approximately the constitution $C_4H_5O_4NAg_2$ is obtained in presence of an excess of ammonia; when treated with ethyl iodide, this yields ethyl *i*-aspartate, together with small amounts of an *N*-ethylated product.

The hydrolysis of the diethyl ester by means of a limited amount of alcoholic potassium hydroxide leads to the formation of a mixture of the diethyl ester and *i*-aspartic acid. No ester was obtained on heating potassium hydrogen *i*-aspartate with ethyl iodide and alcohol at 100°. When heated with alcohol in a sealed tube at 93°, *i*-aspartic acid remains unchanged, but at 150—160° it is partially decomposed, yielding carbon dioxide and an oil from which a product could not be isolated.

G. Y.

Transformations of Methyl Dicarboxyaconitate.

Richard Anschütz and Alphons Deschauer (*Annalen*, 1906, **347**, 1—16).—Methyl dicarboxyaconitate is best prepared from methyl dichloro-oxalate (1 mol.) and methyl sodiomalonate (3 mols.), when the following reaction takes place: $OMe\cdot CCl_2\cdot CO_2Me + 2CHNa(CO_2Me)_2 = 2NaCl + MeOH + C(CO_2Me)_2:C(CO_2Me)\cdot CH(CO_2Me)_2$. The sodium salt of the methyl dicarboxyaconitate is then formed by interaction with 1 mol. of methyl sodiomalonate. The ester is purified by recrystallisation from water, and melts at 62°. At the same time, *methyl ethylenetricarboxylate*, $CH(CO_2Me){:}C(CO_2Me)_2$, is formed as a by-product; it crystallises from methyl alcohol, melts at 134—135°, and does not give a yellow coloration with alkalis as does the aconitate.

Methyl dicarboxytricarballylate,

$$CH(CO_2Me)_2{\cdot}CH(CO_2Me){\cdot}CH(CO_2Me)_2,$$

is prepared by reducing methyl dicarboxyaconitate with zinc dust in acetic acid solution, and forms plates melting at 85—86°. It is completely soluble in alkalis and forms the *monosodium* derivative, $C_{13}H_{17}O_{10}Na$. It may also be prepared from methyl dichloroacetate and methyl sodiomalonate. When boiled with concentrated hydrochloric acid it is quantitatively converted into tricarballylic acid melting at 158°.

The sodium derivative of methyl dicarboxyaconitate forms small, orange-yellow crystals, and when pure yields with methyl iodide *methyl αα-dicarboxy-α-methylaconitate*,

$$C(CO_2Me)_2{:}C(CO_2Me){\cdot}CMe(CO_2Me)_2,$$

which crystallises in needles, melts at 86°, and boils at 208—210° under 12 mm. pressure.

α-Methylaconitic acid, $CH(CO_2H){:}C(CO_2H){\cdot}CHMe{\cdot}CO_2H$, is prepared by heating methyl dicarboxymethylaconitate with 25 per cent. sodium hydroxide at 60—70° and then isolating the methylaconitic acid as the silver salt; it forms small crystals melting and decomposing at 169—172°. The *silver* salt is a white powder.

Methyl dicarboxymethyltricarballylate,

$$CH(CO_2Me)_2{\cdot}CH(CO_2Me){\cdot}CMe(CO_2Me)_2,$$

is obtained by reducing methyl dicarboxymethylaconitate with zinc dust in acetic acid solution, and forms large, transparent crystals melting at 58—59·5°; its *sodium* derivative, $C_{14}H_{19}O_{10}Na$, is obtained as a solid by adding dry benzene to its methyl-alcoholic solution. When methyl dicarboxymethylaconitate is boiled with 20 per cent. hydrochloric acid, it is converted into a mixture of two α-methyltricarballylic acids, $CH_2(CO_2H){\cdot}CH(CO_2H){\cdot}CHMe{\cdot}CO_2H$, which are separated by crystallisation from water. The sparingly soluble acid melts at 178—180°, whilst the more soluble acid melts at 132—134°. The *silver* salt of each acid was prepared, and the acids proved to be identical with those obtained by Auwers, Köbner, and Meyenberg (Abstr., 1892, i, 41). K. J. P. O.

Synthetical Crystalline *l*-Iditol. GABRIEL BERTRAND and A. LANZENBERG (*Compt. rend.*, 1906, **143**, 291—294).—The authors have obtained 28 grams of pure recrystallised *l*-iditol from 300 grams of xylose by the following modification of Fischer and Fay's method (Abstr., 1895, i, 650); the xylose is converted into a mixture of *l*-gulonic and *l*-idonic acids, the latter removed by crystallisation of its lactone, when the mother liquor reduced by sodium amalgam contains *l*-iditol together with a little *l*-sorbitol, which is removed in the form of its benzylidene derivative, and the crystallisation of the *l*-iditol induced by sowing with a crystal of sorbieritol (α-iditol) (compare

Maquenne and Bertrand, Abstr., 1901, i, 497). *l*-Iditol crystallises in rhombic prisms, melts at 73·5°, and has $[\alpha]_D + 3·5°$ in 10 per cent. aqueous solution at 20° [the corresponding constants of *a*-iditol are 73·5° and −3·5° respectively, and not 75° and −3·53° as originally stated (compare Abstr., 1905, i, 21)]; the *hexa-acetyl* derivative crystallises in hexagonal plates, melts at 121·5°, and has $[\alpha]_D + 25·33°$ in 5 per cent. chloroform solution at 20° [the hexa-acetyl derivative of *a*-iditol melts at 121·5° and has $[\alpha]_D - 25·65°$ in 5 per cent. chloroform solution (compare Abstr., 1905, i, 21)]; trimethylene-*l*-iditol crystallises in thin, brilliant needles almost insoluble in alcohol, insoluble in chloroform, soluble in acetic acid, and has $[\alpha]_D$ −36°, and not +8° as stated by Lobry de Bruyn and Alberda van Eckenstein (Abstr., 1900, i, 332). M. A. W.

Action of Ammonium Chloride on Aqueous Sucrose Solutions.

Friedrich Strohmer and O. Fallada (*Chem. Centr.*, 1906, i, 1819; from *Österr.-ung. Zeit. Zucker-Ind. Landw.*, **35**, 168—171).—On heating in various ways aqueous solutions containing sucrose and ammonium chloride in the proportion 3 : 1 or 1 : 1, it is found that the polarisation diminishes to a greater or less extent, the liquid becoming coloured and capable of reducing Fehling's solution. The solution remains neutral, except when heated at 115°, in which case it becomes faintly acid. Assuming that the solution contains invert sugar, Clerget's formula indicates an amount of this sugar corresponding very nearly with the original proportion of sucrose. The hydrolysis of the sucrose must be assumed to be a consequence of the decomposition of the ammonium chloride into ammonia and hydrogen chloride.

T. H. P.

Hydrolysis of Raffinose by means of Citric Acid.

J. Pieraerts (*Chem. Centr.*, 1906, ii, 24—25; from *Bull. Assoc. chim. Sucr. Dist.*, **23**, 1143—1146).—Raffinose is completely resolved into *d*-fructose (lævulose) and melibiose by citric acid, the hydrolytic action of the acid being proportional to its concentration and to the duration of its action. The action of the citric acid may, under certain conditions, proceed further than this first stage, but the lævulose is not attacked until long after the first stage in the hydrolysis of raffinose is reached. T. H. P.

Mechanism of Additive Reactions. VII. Reactivity of Unsaturated Nitrogen.

Daniel Vorländer (*Annalen*, 1906, **345**, 251—260).—The oxidation of amines is initially an additive process (compare Dunstan and Goulding, Trans., 1899, **75**. 1004; Wolffenstein, Abstr., 1900, i, 209; Bamberger, Abstr., 1902, i, 364). In its subsequent stages, the oxidation is influenced chiefly by the groups containing hydrogen adjacent to the nitrogen atom; consequently primary amines are most slowly, and tertiary amines most rapidly oxidised. Ammonium bases, which do not contain unsaturated nitrogen, are stable towards the oxidising agent. The oxidising agent used in these and the following experiments was permanganic acid in the presence of an acid. The latter on the one hand accelerates the oxidising action of the permanganate, and on the other retards oxidation by salt-formation with the amine. In neutral or alkaline solution most amines are instantly oxidised by permanganate. The oxidation is also influenced by temperature, concentration, the presence of easily oxidisable substances which act as catalysts, and even by the products of oxidation.

Acyl derivatives are comparatively stable towards alkaline permanganate, but in acid solution are more easily oxidised than the amines, owing to the absence of salt-formation.

These results are illustrated in the paper by tables and curves.

C. S.

Oxidation of Ammonia Derivatives by Permanganic Acid. Daniel Vorländer, Georg Blau, and Theodor Wallis (*Annalen*, 1906, **345**, 261—276).—The paper gives a detailed account of the results mentioned in the preceding abstract, and is not suitable for abstraction.

The velocity of oxidation of an amine by acidified permanganate under carefully stated conditions is a new constant by which such substances can be identified. C. S.

Combination of Amino-acids derived from Proteids. Albert Morel (*Compt. rend.*, 1906, **143**, 119—121).—When the hydrochloride of ethyl glycine is treated with a large excess of carbonyl chloride in boiling toluene, *ethyl glycine isocyanate*, $CO{\cdot}N{\cdot}CH_2{\cdot}CO_2Et$, is formed. It is a colourless liquid which boils at 115—120° under 15 mm. pressure. With aniline it yields the compound

$$HNPh{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2Et,$$

which melts at 113—114°. When boiled with water, the *iso*cyanate decomposes, carbon dioxide, ethyl alcohol, and carbamidediacetic acid, $CO(NH{\cdot}CH_2{\cdot}CO_2H)_2$, being formed. This acid forms well-developed crystals which melt at 166—168°.

The *iso*cyanate reacts with an alkaline solution of leucine, forming the carbamide derivative,

$$CO_2H{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}CH(CO_2H){\cdot}CH_2Pr^{\beta},$$

which is insoluble in acids and melts and decomposes at 183°.

In a similar manner, with a solution of tyrosine, the *compound* $CO_2H{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}C_6H_4{\cdot}OH$ is formed; it crystallises from alcohol in delicate needles and melts and decomposes at 214°. These compounds do not appear to be hydrolysed under the influence of pepsin and pancreatic juice. H. M. D.

Synthesis of Cyanogen and of Hydrogen Cyanide from their Elements. Theodor Wallis (*Annalen*, 1906, **345**, 353—362).—Contrary to statements in the literature, cyanogen is not produced when electric sparks are passed, or the arc is established, between carbon poles in an atmosphere of nitrogen. In the presence of moisture or of hydrogen, hydrogen cyanide is formed.

In order to detect cyanogen in the presence of hydrogen cyanide, the mixture is passed into an acidified solution of a silver salt, the silver cyanide removed, the silver in the solution precipitated by yellow ammonium sulphide, a few drops of alkali are added, and after filtration and evaporation the test for a thiocyanate is applied. The estimation of cyanogen and hydrogen cyanide is effected by passing the mixture into a solution of potassium hydroxide; the hydrogen cyanide and one-half of the cyanogen is estimated as silver cyanide; the other half, now present as potassium cyanate, is determined by boiling the cyanate with dilute sulphuric acid and titrating the ammonia produced. An alternative method is to pass the mixture into a solution of ammonium hydroxide or carbonate. After titration with a silver solution, the ammonium cyanate is converted into carbamide, and isolated and weighed as such.

Cyanogen prepared in the usual way always contains hydrogen cyanide, which can be removed by passing the gas over cotton-wool moistened with a silver solution. C. S.

Action of the Electric Discharge on Cyanogen. H. Gaudechon (*Compt. rend.*, 1906, **143**, 117—119).—When cyanogen is subjected to the action of the electric discharge, nitrogen is liberated and a solid, brown substance is formed. The composition of the deposit varies with the pressure of the gas, the capacity of the apparatus, and the potential of the discharge. It is partially, sometimes completely, soluble in water and ethyl alcohol, and always dissolves readily in dilute alkali solutions, and therefore does not contain free carbon. When heated carefully to dark redness, the solid substance gives off nitrogen, and the residue is found to be insoluble even in strong alkali solutions. The author points out that the products of the action of the discharge are thus conclusively proved to be condensation products containing excess of carbon, and do not result from the simple polymerisation of cyanogen. H. M. D.

Carbonyl Bromide. A. von Bartal (*Annalen*, 1906, **345**, 334—353).—Emmerling and Lengyel's (Abstr., 1880, 627) or Besson's (Abstr., 1895, i, 317) methods are unsuitable for the preparation of pure carbonyl bromide. The boron tribromide required in the latter method is conveniently obtained in 60—70 per cent. yield by passing bromine vapour over powdered boron containing 10 per cent. of magnesium at a dull red heat.

Carbonyl bromide is obtained in small quantities directly from carbon monoxide and bromine vapour in the presence of aluminium bromide, or by the silent electric discharge. It is prepared in 50—60 per cent. yield by allowing sulphuric acid of sp. gr. 1·84 to drop slowly into carbon tetrabromide at 160—170°. The red distillate is shaken with mercury, distilled, shaken again with powdered antimony, and once again distilled. Pure carbonyl bromide is a heavy, mobile, colourless liquid which fumes in air, and smells somewhat like phosgene. It boils and decomposes slightly at 64—65°, has a sp. gr. 2·45 at 15°, and is decomposed by light or heat. With dimethylaniline and zinc bromide or aluminium bromide it forms dyes of the crystal-violet group, particularly hexamethyl-*p*-rosaniline hydrobromide; in the absence of the contact substance, *p*-bromodimethylaniline is produced. It is more stable towards water than carbonyl chloride. C. S.

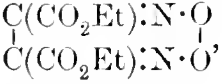
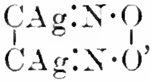
Preparation of Cyanamides. RALPH H. MCKEE (*Amer. Chem. J.*, 1906, **36**, 208—213).—Dipropylcyanamide is obtained in a 93 per cent. yield by shaking 1·1 mols. of bromine in light petroleum solution with 1 mol. of dipropylamine and 4·5 mols. of potassium cyanide in aqueous solution below 15°. When heated with sodium methoxide in methyl-alcoholic solution at 65°, it forms as-*ψ-methyldipropylcarbamide*, $OMe{\cdot}C(NH){\cdot}NPr_2$, which is obtained in a yield of 80 per cent.; it boils at 98° under 19 mm., or at 203° under 748 mm. pressure, has a sp. gr. 0·9103 at 22°/4°, and is more soluble in cold than in hot water.

In a similar manner, di*iso*butylcyanamide, boiling at 123° under 25 mm. pressure, is obtained in an 83 per cent., di*iso*amylcyanamide, boiling at 134° under 14 mm. pressure, in a 92 per cent., dimethylcyanamide, boiling at 98° under 104 mm. pressure, in a 50 per cent., ethylcyanamide in a 71 per cent., benzylcyanamide, melting at 43° (33°: Strakosch, this Journal, 1872, **25**, 1026), in a 90 per cent., and *cyanopiperidine*, $C_5NH_{10}{\cdot}CN$, boiling at 102° under 11 mm. pressure, in an 80 per cent. yield. iso*Amylcyanamide*, $C_5H_{11}{\cdot}NH{\cdot}CN$, prepared by this method, was analysed.

Diethylcyanamide is obtained in a good yield if ethyl acetate is used in place of light petroleum, and the temperature maintained about 5°. as-*ψ-Methyldiethylcarbamide*, $OMe{\cdot}C(NH){\cdot}NEt_2$, boils at 171—172° under 745 mm. pressure, distils with water, benzene, or ether vapour, is a strong base, and can be titrated with hydrochloric acid.

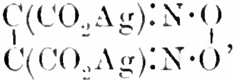
G. Y.

Constitution of Fulminic Acid. MILORAD Z. JOVITSCHITSCH (*Annalen*, 1906, **347**, 233—247).—The formulæ suggested by various investigators for fulminic acid are discussed, and it is pointed out that Nef's formula, $C{:}NOH$, is not in accord with the fact that an unsaturated compound is formed in an extremely violent reaction by the action of nitric acid on alcohol. It is thought rather that Scholl's formula,  $\begin{array}{l}CH{:}N{\cdot}O\\ |\qquad\ \ \ |\\ CH{:}N{\cdot}O\end{array}$, which represents the substance as glyoxime peroxide, is correct, and attempts have been made to synthesise the compound and thus solve the question of its constitution.

From the peroxide of ethyl di*iso*nitrososuccinate (ethyl glyoxime peroxide-dicarboxylate),  $\begin{array}{l}C(CO_2Et){:}N{\cdot}O\\ |\qquad\qquad\quad\ \ |\\ C(CO_2Et){:}N{\cdot}O\end{array}$, the silver salt of the dioxime peroxide,  $\begin{array}{l}CAg{:}N{\cdot}O\\ |\qquad\quad\ \ |\\ CAg{:}N{\cdot}O\end{array}$, was obtained. It resembles silver fulminate extremely closely, but differs from it in being easily soluble in nitric acid and in being less explosive.

Ethyl glyoxime-peroxide-dicarboxylate (*ethyl azodioxazinedicarboxylate*) is obtained in quantitative yield by preparing the nitrolic acid of ethyl acetoacetate, $OHN{:}C(NO_2){\cdot}CO_2Et$ (Abstr., 1892, 699), and simply evaporating its ethereal solution, when nitrous acid is eliminated and the peroxide formed.

The corresponding acid is obtained from the ester by dissolving it in concentrated sulphuric acid, and then pouring into water and extracting the oil which separates with ether; the crystalline acid melts at 96°; its alkali salts are extremely soluble, but the *silver* salt,

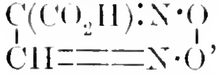


$$\begin{array}{l} C(CO_2Ag){:}N\cdot O \\ \quad | \qquad\qquad\ \ | \\ C(CO_2Ag){:}N\cdot O \end{array},$$

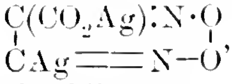
is a yellowish-white powder, which is very sensitive to light and somewhat explosive.

In this hydrolysis an oil is also formed which may be an ethyl oximidoacetate, $OH\cdot N{:}CH\cdot CO_2Et$.

Glyoxime-peroxide-carboxylic acid (*azdioxazinecarboxylic acid*),



$$\begin{array}{l} C(CO_2H){:}N\cdot O \\ \quad | \qquad\qquad | \\ CH{=\!=\!=}N\cdot O \end{array},$$

is prepared by hydrolysing the peroxide ester with sulphuric acid and dissolving the insoluble product in sodium hydroxide; it forms a thick, pale syrup, extremely soluble in water, and when treated with silver nitrate yields a yellow, extremely explosive silver salt, which is not affected by light. When the sodium salt, which is prepared by precipitating the strongly alkaline solution of the acid with alcohol, is treated with silver nitrate, the *silver* salt,  $\begin{array}{l} C(CO_2Ag){:}N\cdot O \\ | \qquad\qquad\quad | \\ CAg{=\!=\!=}N{-}O \end{array}$, is formed, and exceeds all hitherto described salts in explosibility.

The *silver glyoxime peroxide* (*silver azdioxazine*) is prepared by treating ethyl glyoxime-peroxide-dicarboxylate with 25 per cent. sodium hydroxide under accurately defined conditions; both a *mono*- and a *di-sodium* salt can be obtained, from which both *mono*- and *di-silver* salts are prepared. The di-silver salt is a yellow powder which is not sensitive to light and is stable in the air. When treated with concentrated hydrochloric acid or heated on platinum it explodes violently. When boiled for some time with dilute hydrochloric acid, hydroxylamine is formed; but if the salt is dissolved in dilute nitric acid and hydrochloric acid then added, glyoxime peroxide can be isolated.

K. J. P. O.

Ureides. I. Action of Urethane on Pyruvic Acid and its Derivatives. Louis J. Simon (*Ann. Chim. Phys.*, 1906, [viii], **8**, 467—501).—A more detailed account of work already published (Abstr., 1902, i, 14).

G. S.

Researches in the *cyclo*Hexane Series. Paul Freundler (*Bull. Soc. chim.*, 1906, [iii], **35**, 539—551).—The results recorded have, for the most part, already appeared (Freundler and Damond, Abstr., 1905, i, 890, and Freundler, this vol., i, 283). The present two papers give experimental details of the methods of preparation employed.

When iodo*cyclo*hexane is heated with ethyl sodioacetoacetate in presence of alcohol, only traces of ethyl *cyclo*hexylacetoacetate are produced, the principal product being *cyclo*hexene. When the alcohol is replaced by xylene, scarcely any action occurs.

It was found impossible to prepare pure hexahydrobenzyl chloride by the action of hydrogen chloride or phosphorus pentachloride on the corresponding alcohol. Similar attempts to prepare hexahydrobenzyl bromide were also unsuccessful.

Acetonitrile condenses with magnesium hexahydrobenzyl iodide, yielding methyl*cyclo*hexane, a white solid containing nitrogen, and di*cyclohexylethane*, $C_{14}H_{26}$, a viscous, pleasant-smelling liquid, which boils at 145—150° under 20 mm. and at 263—264° under 762 mm. pressure.

A specimen of magnesium hexahydrobenzyl bromide, containing some hexahydrobenzyl alcohol, was condensed with ethyl acetate, and yielded a *product* boiling at 202—205° under 45 mm. pressure, which may be the alcohol $(C_6H_{11}\cdot CH_2)_2\cdot CMe\cdot OH$. When warmed with oxalic acid at 140—150°, this was transformed into an unsaturated hydrocarbon, boiling at 143—147° under 12—13 mm. pressure. T. A. H.

Reduction of Nitro-compounds by Tin Haloids. II. HEINRICH GOLDSCHMIDT and EINAR SUNDE (*Zeit. physikal. Chem.*, 1906, **56**, 1—42. Compare Abstr., 1904, ii, 608).—The method described previously has been further used in the study of *m*- and *o*-nitrophenols, *o*- and *p*-nitrobenzenesulphonic acids, and *o*- and *m*-nitrobenzaldehyde. The behaviour of the nitrophenols and of *m*-nitrobenzaldehyde is normal, but that of the other substances named is not so strictly in harmony with the rules deduced in the earlier paper. In the case of the two nitrobenzenesulphonic acids, it is found that an increase in the hydrochloric acid concentration is accompanied by an increase in the velocity of reduction which is greater than that required by the rule of proportionality (*loc. cit.*). Similar deviations from this rule have been observed in the case of *o*-nitrobenzaldehyde. Further, whilst the other nitro-compounds studied require 3 mols. of stannous salt for each nitro-group, it is found that *o*-nitrobenzaldehyde reacts with 2 mols. of stannous salt, and reduction beyond that stage takes place with extreme slowness, owing to the production of anthranil.

The authors' experiments show that in the reduction of nitro-compounds a part of the hydrochloric acid may be replaced by metallic chlorides without appreciably affecting the velocity of reduction. Thus the rate of reduction of *m*-nitrobenzenesulphonic acid is the same whether the solution is $N/1$ with regard to hydrochloric acid or $N/2$ with regard to hydrochloric acid and, at the same time, $N/2$ with regard to sodium or barium chloride. This observation leads to the view that the ion which is active in all these reduction processes is $SnCl_3'$ (compare *loc. cit.*).

The above-mentioned behaviour of *o*-nitrobenzaldehyde furnishes support to Haber's view of the stages in the reduction of nitro-compounds: namely, (1) $R\cdot NO_2 \rightarrow R\cdot NO$, (2) $R\cdot NO \rightarrow R\cdot NH\cdot OH$, (3) $R\cdot NH\cdot OH \rightarrow R\cdot NH_2$. The authors find that while change (2) takes place apparently in all cases with extreme rapidity, the velocity of change (3), although considerably greater than that of change (1), is measurable in many cases; the laws regulating the velocity of change (3) appear to be similar to those regulating the velocity of change (1). The substitution of $SnBr_2 + HBr$ for $SnCl_2 + HCl$, which makes the reduction change (1) eight times as rapid, makes the reduction change (3) about four times as rapid. J. C. P.

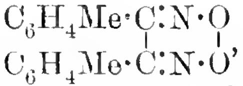
New Method of preparing the so-called Primary Dinitrohydrocarbons. Giacomo Ponzio (*Atti R. Accad. Lincei*, 1906, [v], **15**, ii, 42—45 and 118—128).—The ordinary methods for preparing dinitro-derivatives of aliphatic hydrocarbons cannot be employed for obtaining primary dinitrohydrocarbons containing a complicated aromatic group. The latter compounds can, however, be prepared by the action of nitrogen tetroxide on ethereal solutions of the oximes (this vol., i, 593). In this way the author has obtained phenyldinitromethane, *p*-tolyldinitromethane, anisyldinitromethane, and piperonyldinitromethane.

The statement, based on the work of Scholl (Abstr., 1891, 315) and Beckmann (Abstr., 1889, 980), that the action of nitrogen tetroxide on aromatic aldoximes yields peroxides of the aldoximes, which then undergo transformation into peroxides of the dioximes, is erroneous. Only in the cases of benzaldoxime and *p*-tolualdoxime are small proportions of these peroxides formed.

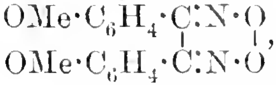
Regarding the primary dinitro-hydrocarbons as nitrohydroxamic acids (Abstr., 1903, i, 786), their formation by the interaction of nitrogen tetroxide and oximes may be represented by the scheme :

$$H\cdot CPh{:}NOH \longrightarrow OH\cdot CPh{:}NOH \longrightarrow NO_2\cdot O\cdot CPh{:}NOH.$$

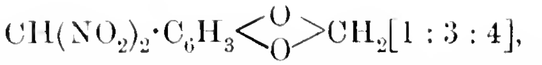
p-*Tolualdoxime peroxide*, $C_6H_4Me\cdot CH{:}N\cdot O\cdot O\cdot N{:}CH\cdot C_6H_4Me$, prepared as described above, and also by passing nitrous acid vapours into an ethereal solution of *p*-tolualdoxime, crystallises from chloroform in shining, white plates, decomposes with a slight explosion at 121°, and dissolves in benzene.

p-*Tolildioxime peroxide*,  $\begin{array}{l} C_6H_4Me\cdot C{:}N\cdot O \\ \qquad\qquad\ \ | \qquad | \\ C_6H_4Me\cdot C{:}N\cdot O \end{array}$, crystallises from alcohol in shining, white needles, melts at 143°, and dissolves in ether, chloroform, or benzene, and, to a slight extent, in light petroleum.

p-*Tolyldinitromethane*, $C_6H_4Me\cdot CH(NO_2)_2$, crystallises from light petroleum in white plates melting at 77°, and dissolves in all the ordinary organic solvents ; when heated at about 130°, it yields *p*-toluic acid. The *potassium* derivative, $C_6H_4Me\cdot C(NO_2){:}NO_2K$, crystallises from alcohol in yellow laminæ and dissolves readily in water. The *silver* derivative, $C_8H_7O_4N_2Ag$, separates from water in yellow needles and is stable under the action of light.

Anisildioxime peroxide,  $\begin{array}{l} OMe\cdot C_6H_4\cdot C{:}N\cdot O \\ \qquad\qquad\qquad\ | \qquad | \\ OMe\cdot C_6H_4\cdot C{:}N\cdot O \end{array}$, crystallises from alcohol in shining, white needles, melting at 113°, and dissolves in light petroleum, ether, chloroform, or benzene.

Anisyldinitromethane, $OMe\cdot C_6H_4\cdot CH(NO_2)_2$, crystallises from light petroleum in slender needles, melting at 34°, and dissolves readily in all the ordinary organic solvents ; when heated at about 130°, it gives anisic acid. The *potassium* derivative, $OMe\cdot C_6H_4\cdot C(NO_2){:}NO_2K$, crystallises from water in red laminæ, which, if left in the mother liquor, rapidly change to a mass of yellow prisms. The *silver* derivative, $C_8H_7O_5N_2Ag$, separates from water in orange-yellow plates, which remain unchanged in the light.

Piperonyldinitromethane,  $CH(NO_2)_2\cdot C_6H_3{<}\substack{O\\O}{>}CH_2[1:3:4]$, crystallises from light petroleum in white plates, melts at 72°, and decomposes at about 130° with evolution of red vapours. The *potassium* derivative, $C_8H_5O_6N_2K$, forms yellow prisms, soluble in water and sparingly so in alcohol.

The *silver* derivative, $C_8H_5O_6N_2Ag$, crystallises from water in red needles stable towards light. T. H. P.

Hydrolysis of Methyl Benzenesulphonate. II.

ARTUR PRAETORIUS (*Monatsh.*, 1906, **27**, 465—485. Compare Abstr., 1905, i, 186).—The hydrolysis of methyl benzenesulphonate by water, as also its conversion into a methyl haloid and benzenesulphonic acid by the action of a hydrohaloid acid or its salts, are side-reactions. Of these the latter is a reaction of the halogen anion, as is shown by the equivalence of the amounts of the products, and it is not accelerated by the presence of hydrogen ions.

The results obtained agree with Wegscheider's formula for the hydrolysis of esters (Abstr., 1902, ii, 493). G. Y.

Nitration of Aromatic Arylsulphonamides.

AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 163516).—The nitro-derivatives of aromatic arylsulphonamides formerly described (Abstr., 1905, i, 639) are readily obtained by nitrating in the presence of a suitable organic solvent, such as alcohol, acetone, or benzene. When the solvent is not miscible with nitric acid, vigorous agitation is necessary.

C. H. D.

Preparation of Hydroxyethylaniline and its Derivatives.

BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 163043).—Hydroxyethylaniline and similar compounds are obtained in good yield by heating aromatic amines with ethylene chlorohydrin and water. One mol. of the chlorohydrin and 2 mols. of the amine may be used, or the excess of the latter may be replaced by sodium acetate or carbonate. Thus aniline yields hydroxyethylaniline (Knorr, Abstr., 1889, 1218).

Hydroxyethylaniline-o-carboxylic acid,

$$OH\cdot CH_2\cdot CH_2\cdot NH\cdot C_6H_4\cdot CO_2H,$$

prepared from anthranilic acid, crystallises from benzene in needles and melts at 143°.

Hydroxyethyl-o-toluidine, $OH\cdot CH_2\cdot CH_2\cdot NH\cdot C_6H_4Me$, forms a colourless oil and boils at 285—286°. C. H. D.

Compounds of Wool with Colourless Amines and Acids.

DANIEL VORLÄNDER and A. J. PEROLD (*Annalen*, 1906, **345**, 288—302).—The absorption of amines and acids by wool is similar to other chemical additive processes. In the series aniline, chloroaniline, and dichloroaniline hydrochlorides, the amount of the absorption is in the same order as the dissociation of the salt. The same holds true after the addition of hydrochloric acid, acetic acid, or acetic acid and sodium acetate, the absorption of amine being greatest in the last case.

The absorption of different acids is not in the order of their relative strengths, probably because in a heterogeneous system adsorption, diffusion, capillarity, &c., play a part in the additive process. With acids of similar chemical character, however, the amount of absorption is in the order of their conductivities.

Neutral salts are not absorbed by wool, but potassium hydroxide, tetramethylammonium hydroxide, and *p*-benzeneazophenyltrimethylammonium hydroxide are very readily taken up.

There is not any essential difference between the absorption by wool or silk of coloured and colourless substances.

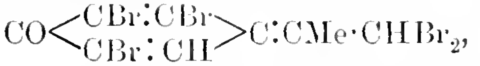
Extensive tables are given in the paper. C. S.

Action of Bromine and Chlorine on Phenols. Substitution Products, ψ-Bromides, and ψ-Chlorides. XVI. Hexabromo-ψ-bromide of *p-iso*Propylphenol.

THEODOR ZINCKE (*Annalen*, 1906, **349**, 67—82. Compare this vol., i, 172).—ψ-p-*Tribromo*iso*propyltribromophenol* (ψ-*hexabromo*-p-iso*propylphenol*),

$$\mathrm{CO}<\begin{matrix}\mathrm{CBr{:}CBr}\\ \mathrm{CBr{:}CH}\end{matrix}>\mathrm{CH{\cdot}CBrMe{\cdot}CHBr_2}$$

or $OH{\cdot}C_6HBr_3{\cdot}CBrMe{\cdot}CHBr_2$, is obtained by treating finely-powdered 3 : 5 : 3′ : 5′-tetrabromo-*p*-diphenoldimethylmethane (*loc. cit.*) with a slight excess of bromine for twenty-four hours. It crystallises in colourless plates or prisms and melts at 115—116°. Cold solutions of sodium hydroxide or carbonate do not react appreciably; water acting on the substance in acetone produces pentabromo*iso*propylidenequinone. Cold acetic anhydride and concentrated sulphuric acid produce the *acetyl* derivative, $C_{11}H_8O_2Br_6$, which melts at 133—134° and is easily hydrolysed in cold alcoholic solution, yielding by loss of hydrogen bromide pentabromo-*p*-*iso*propylenephenol (see below). When the ψ-hexabromide is boiled with acetic anhydride it yields tetrabromo-*p*-*iso*propenylphenol acetate (see below), in addition to the normal acetyl derivative.

p-*Dibromo*iso*propylidenetribromoquinone* (*pentabromo*iso*propylidenequinone*),  $\mathrm{CO}<\begin{matrix}\mathrm{CBr{:}CBr}\\ \mathrm{CBr{:}CH}\end{matrix}>\mathrm{C{:}CMe{\cdot}CHBr_2}$, is prepared by shaking an ethereal solution of the ψ-hexabromide with an equal volume of 10 per cent. sodium acetate, or as above. It separates from ether in glistening, golden-yellow needles and melts at 143—144°, and with hydrogen bromide regenerates the ψ-hexabromide.

a-Dibromo-β-acetoxy-p-iso*propyltribromophenol acetate*,

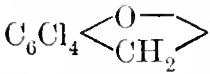
$$OAc{\cdot}C_6HBr_3{\cdot}CMe(OAc){\cdot}CHBr_2,$$

is precipitated by the addition of water to the colourless solution obtained by treating the preceding quinone with cold acetic anhydride and concentrated sulphuric acid. It separates from methyl alcohol in thick, glistening, rhombic plates, melts at 127°, and by hydrolysis yields p-*dibromo*iso*propenyltribromophenol* (*pentabromo*-p-iso*propenylphenol*), $OH{\cdot}C_6HBr_3{\cdot}CMe{:}CBr_2$, which melts at 143—144°. The last-mentioned compound is also obtained when the isomeric quinone is allowed to remain in acetone or is reduced by alkaline stannous chloride; the *acetyl* derivative, $C_{11}H_7O_2Br_5$, melts at 104—105°.

p-*Bromo*iso*propenyltribromophenol* (*tetrabromo*-p-iso*propenylphenol*), $OH{\cdot}C_6HBr_3{\cdot}CMe{:}CHBr$, is obtained by the hydrolysis of the tetrabromoacetate prepared from the ψ-hexabromide, or by the reduction of the pentabromoquinone by stannous chloride in glacial acetic acid. It crystallises in colourless needles, melts at 98—99°, combines with bromine to form, in the cold the ψ-hexabromide, or at 100° the ψ-heptabromide (*loc. cit.*); its acetyl derivative separates from alcohol in rhombic leaflets, melts at 126—127°, and is identical with the acetate obtained from the ψ-hexabromide by boiling acetic anhydride. C. S.

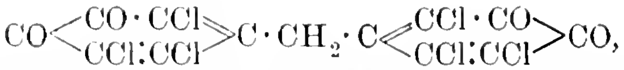
Action of Tertiary Amines on Tetrachloro-*p*-cresol ψ-Bromide. XVII.

THEODOR ZINCKE and L. HUNKE (*Annalen*, 1906, **349**, 83—98).—2 : 3 : 5 : 6-*Tetrachloro-4-hydroxybenzylpyridinium bromide*, $OH\cdot C_6Cl_4\cdot CH_2\cdot C_5NH_5Br$, obtained from tetrachloro-*p*-cresol ψ-bromide and pyridine in ethereal solution, separates from hot glacial acetic acid in leaflets and melts and decomposes at 231°. It forms with bromine water in acetic acid glistening, yellow leaflets of a *perbromide*, with potassium dichromate a yellow, crystalline precipitate, and with potassium iodide a violet-brown, glistening *periodide*. The *platinichloride*, $(C_{12}H_7ONCl_4)_2,H_2PtCl_6$, forms yellow crystals.

The betaine derivative of 2 : 3 : 5 : 6-*tetrachloro-4-hydroxybenzyltrimethylammonium hydroxide*,  $C_6Cl_4<\overset{O}{\underset{CH_2}{}}>NMe_3$, results when tetrachloro-*p*-cresol ψ-bromide in ether is treated with the calculated quantity of 30 per cent. aqueous trimethylamine. It forms a white, crystalline powder, melts and decomposes at 186°, is stable towards aqueous alkali hydroxides, but is converted by hot alcoholic solutions into tetrachloro-*p*-hydroxybenzyl ethyl ether (Abstr., 1902, i, 282).

2 : 3 : 5 : 6-*Tetrachloro-4-hydroxy-4′-diethylaminodiphenylmethane hydrobromide*, $OH\cdot C_6Cl_4\cdot CH_2\cdot C_6H_4\cdot NEt_2,HBr$, is obtained when the ψ-bromide is treated with a small excess of diethylaniline in ether, and forms white needles which melt and turn red at 257—258°. The free *base*, $C_{17}H_{17}ONCl_4$, melts at 135° and forms the corresponding salts with hydrogen chloride or bromide in glacial acetic acid. The base is stable towards hot hydrochloric acid, and is decomposed by hot dilute alkalis, diethylaniline and tarry products being formed. The *acetyl* compound forms colourless needles and melts at 120°.

*Octachloro-*p*-diphenolmethane*, $OH\cdot C_6Cl_4\cdot CH_2\cdot C_6Cl_4\cdot OH$, is obtained by the action of 5 per cent. sodium hydroxide on tetrachloro-*p*-cresol ψ-bromide, of water at 130—140°, or of 5—20 per cent. sodium hydroxide on the pyridinium bromide (with 1 per cent. sodium hydroxide the chief product is tetrachloro-*p*-hydroxybenzyl alcohol), or of concentrated sulphuric acid on tetrachloromethylenequinone, tetrachlorotoluquinol, or the isomeric tetrachloro-*p*-hydroxybenzyl alcohol (compare Abstr., 1902, i, 282; 1903, i, 760, in which the product is regarded as a derivative of dihydroxystilbene). Octachloro-*p*-diphenolmethane forms colourless needles and melts at 279°; and the *acetyl* derivative, $C_{17}H_8O_4Cl_8$, at 257—258°. Nitric acid of sp. gr. 1·4 in glacial acetic acid solution converts the diphenolmethane into tetrachloro-*p*-quinone, whereas with acid of sp. gr. 1·5 at a gentle heat the chief product is an *o-quinone*,

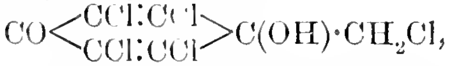

$$CO<\begin{matrix}CO\cdot CCl\\CCl{:}CCl\end{matrix}>C\cdot CH_2\cdot C<\begin{matrix}CCl\cdot CO\\CCl{:}CCl\end{matrix}>CO,$$

which separates from benzene in dark red crystals and dissolves in alkalis with a greenish-blue colour changing to brown (compare Abstr., 1899, i, 616).

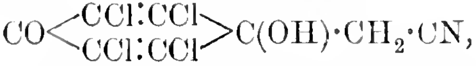
Bromine at 150° reacts with the diphenolmethane to form a mixture of substances which melts at 261° and behaves like a ψ-bromide.

C. S.

Tetrachloro-*p*-cresol-ψ-chloride. XVIII. THEODOR ZINCKE and KARL BÖTTCHER (*Annalen*, 1906, **349**, 99—106. Compare Abstr., 1902, i, 282; this vol., i, 166).—*Tetrachloro*-p-*cresol-ψ-chloride*,
$OH\cdot C_6Cl_4\cdot CH_2Cl$
or  $CO<\begin{matrix}CCl{:}CCl\\CCl{:}CCl\end{matrix}>CH\cdot CH_2Cl$, results when tetrachloro-*p*-hydroxybenzyl alcohol is heated at 100° with an excess of hydrogen chloride in glacial acetic acid, or by chlorinating tetrachloro-*p*-cresol at 150—180°. It crystallises in long needles, melts at 145—146°, and behaves like the corresponding ψ-bromide (*loc. cit.* and preceding abstract). The *acetyl* derivative, $OAc\cdot C_6Cl_4\cdot CH_2Cl$, melts at 118—119°, and by boiling with acetic anhydride and sodium acetate yields the diacetate of tetrachloro-*p*-hydroxybenzyl alcohol.

ω-2 : 3 : 5 : 6-*Pentachlorotolu-ψ-quinol*,  $CO<\begin{matrix}CCl{:}CCl\\CCl{:}CCl\end{matrix}>C(OH)\cdot CH_2Cl$, obtained from the ψ-chloride by the action of nitric acid of sp. gr. 1·4, forms colourless needles, melts at 137—138°, is soluble in alkali hydroxides, and by warming with sodium carbonate yields the oxide described previously (Abstr., 1902, i, 283). The *acetyl* compound, $C_9H_5O_3Cl_5$, forms colourless needles and melts at 128°.

Tetrachloro-p-*hydroxybenzyl cyanide*, $OH\cdot C_6Cl_4\cdot CH_2\cdot CN$, obtained from the ψ-chloride and potassium cyanide in aqueous acetone, separates from dilute acetic acid in leaflets or needles, melts at 208—210°, yields an *acetyl* compound melting at 140—142°, and is hydrolysed by dilute sulphuric acid (3 : 2) at 170—180°, yielding *tetrachloro*-p-*hydroxyphenylacetic acid*, $OH\cdot C_6Cl_4\cdot CH_2\cdot CO_2H$, which melts and decomposes at 240—242°. The cyanide is converted by nitric acid of sp. gr. 1·51 into the *ψ-quinol*,


$$CO<\begin{matrix}CCl{:}CCl\\CCl{:}CCl\end{matrix}>C(OH)\cdot CH_2\cdot CN,$$

which crystallises in needles, melts and decomposes at 200—202°, and yields an *acetyl* derivative which melts and decomposes at 168°.

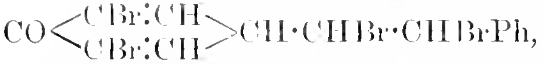
C. S.

Bromine Derivatives of *p*-Hydroxystilbene. XIX. THEODOR ZINCKE and W. GEIBEL (*Annalen*, 1906, **349**, 107—123).—p-*Hydroxy-α-phenylcinnamic acid*, $OH\cdot C_6H_4\cdot CH{:}CPh\cdot CO_2H$, is obtained from *p*-hydroxybenzaldehyde, sodium phenylacetate, and acetic anhydride, the resulting acetyl compound being hydrolysed. The acid forms small, white needles, melts at 223° with loss of carbon dioxide, and gives an *acetyl* derivative, $C_{17}H_{14}O_4$, which melts at 174°; the *methyl* ester melts at 168—169°, and its *acetyl* derivative, $C_{18}H_{16}O_4$, at 108°.

p-*Hydroxystilbene*, $OH\cdot C_6H_4\cdot CH{:}CHPh$, results when the preceding acid is heated rapidly to its melting point; unchanged acid is removed by sodium carbonate, and the residue, after treatment with dilute acid, is crystallised from benzene or glacial acetic acid. It separates in white leaflets, melts at 189°, and forms sparingly soluble *sodium* and *potassium* salts; the *acetyl* compound, $C_{16}H_{14}O_2$, melts at 152°.

3 : 5-*Dibromo-4-hydroxystilbene ψ-dibromide*,

$$OH\cdot C_6H_2Br_2\cdot CHBr\cdot CHBrPh$$

or 
$CO<\begin{matrix}CBr{:}CH\\CBr{:}CH\end{matrix}>CH\cdot CHBr\cdot CHBrPh$, obtained from bromine and *p*-hydroxystilbene in glacial acetic acid, crystallises in white needles, darkens at 192°, and melts and decomposes at 201°. With methyl or ethyl alcohol it yields an oily product, $OH\cdot C_6H_2Br_2\cdot CH(OR)\cdot CHBrPh$ (where $R = Me$ or Et). The *acetyl* derivative, $C_{16}H_{12}O_2Br_4$, obtained with acetic anhydride and concentrated sulphuric acid, forms glistening leaflets and melts at 182°.

1-*Bromophenylethylidene*-3 : 5-*dibromoquinone*,


$$CO<\begin{matrix}CBr{:}CH\\CBr{:}CH\end{matrix}>C{:}CH\cdot CHBrPh,$$

formed spontaneously from the ψ-bromide in aqueous acetone, or in ethereal solution by the action of 10 per cent. aqueous sodium acetate, is an amorphous, yellow powder, which sinters at 140° and melts and decomposes at 190°; with hydrogen bromide in glacial acetic acid the ψ-bromide is regenerated.

3 : 5-*Dibromo-4-hydroxystilbene bromohydrin*,

$$OH\cdot C_6H_2Br_2\cdot CH(OH)\cdot CHBrPh,$$

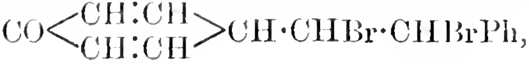
results by the slow addition of water to the ψ-bromide in acetone; it crystallises in white needles, melts at 170°, and with acetic anhydride and sulphuric acid yields the *diacetate* described subsequently.

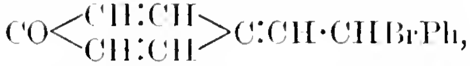
The *acetyl* compound, 
$CO<\begin{matrix}CBr{:}CH\\CBr{:}CH\end{matrix}>CH\cdot CH(OAc)\cdot CHBrPh$, obtained by shaking the ψ-bromide with sodium acetate and glacial acetic acid, forms a white powder, melts at 135°, yields the preceding compound on hydrolysis, and by treatment with sodium acetate and acetic anhydride forms the *diacetate*, $OAc\cdot C_6H_2Br_2\cdot CH(OAc)\cdot CHBrPh$, which melts at 142—143°.

3 : 5-*Dibromo-4-hydroxystilbene*, $OH\cdot C_6H_2Br_2\cdot CH{:}CHPh$, obtained from the ψ-bromide in acetone with excess of stannous chloride, crystallises in needles, melts at 150°, forms sparingly soluble salts with alkalis, yields an *acetyl* compound which melts at 130—131°, and regenerates the ψ-bromide by treatment with bromine in glacial acetic acid.

The *pyridinium bromide*, $OH\cdot C_6H_2Br_2\cdot CH(C_5NH_5Br)\cdot CHBrPh$, formed from the ψ-bromide and pyridine in ether, melts at 145—165°. It dissolves easily in alcohol, acetone, or glacial acetic acid, but quickly separates in the form of a white, sparingly soluble, crystalline powder, which melts and decomposes at 194°. Alkalis decompose it, yielding pyridine and an amorphous, red substance.

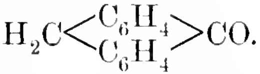
p-*Hydroxystilbene ψ-dibromide*, $OH\cdot C_6H_4\cdot CHBr\cdot CHBrPh$ or

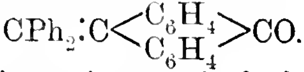

$$CO<\begin{matrix}CH{:}CH\\CH{:}CH\end{matrix}>CH\cdot CHBr\cdot CHBrPh,$$

is prepared by the action, in the dark, of the requisite quantity of bromine in ether on *p*-hydroxystilbene in ether at −15°; it is an unstable, white powder which turns brown at 155°, melts and decomposes at 161°, and does not readily yield pure derivatives. The *acetate*, obtained by acetic anhydride and sulphuric acid, crystallises well in needles and melts and decomposes at 190—192°, decomposition beginning at 180°. The *quinone*,  $CO<{CH:CH \atop CH:CH}>C:CH\cdot CHBrPh$, obtained in a similar manner to the preceding quinone, is an amorphous, yellow powder, becoming white in air; it is readily soluble in the usual solvents, but cannot be crystallised. By reduction with stannous chloride in acetone it yields *p*-hydroxystilbene. The *pyridinium bromide*, $OH\cdot C_6H_4\cdot CH(C_5NH_5Br)\cdot CHBrPh$, is easily soluble in alcohol, ether, or glacial acetic acid, but separates from the last solvent in a sparingly soluble modification which crystallises from hot alcohol in white needles and melts and decomposes at 175°. C. S.

4-Acetylamino-2-aminophenol-6-carboxylic Acid. LEOPOLD CASSELLA & Co. (D.R.-P. 163186).—*p*-Aminosalicylic acid is acetylated, nitrated in sulphuric acid solution, and reduced with iron and acetic acid. The 4-*acetylamino*-2-*aminophenol*-6-*carboxylic acid* thus obtained crystallises from water in sparingly soluble needles, melts at 220°, and forms a sparingly soluble, yellow *diazonium* compound. C. H. D.

4-Acetylamino-2-aminophenol-6-sulphonic Acid. LEOPOLD CASSELLA & Co. (D.R.-P. 163185).—When *p*-acetylaminophenol is dissolved in sulphuric acid at 95°, an *o*-sulphonic acid is formed quantitatively. Nitric and sulphuric acids at 0° convert it into 2-*nitro*-4-*acetylaminophenol*-6-*sulphonic acid*, which on reduction yields the *aminosulphonic acid*, separating from water in sparingly soluble, colourless needles and forming readily soluble salts. C. H. D.

Condensation with Anthranol. R. PADOVA (*Compt. rend.*, 1906, **143**, 121—123).—Anthranol sometimes behaves as if it had the constitution of anthrone,  $H_2C<{C_6H_4 \atop C_6H_4}>CO$. Experiments have now been made to obtain anthrone derivatives by condensation from anthranol. When heated with benzoyl chloride in pyridine solution, anthranol yields anthraquinone and *benzoylanthranol*, which forms white needles melting at 163—165°.

Attempts to condense anthranol with aniline, dimethylaniline, and benzophenone gave no result, but when heated with chlorobenzophenone in xylene solution, hydrogen chloride is evolved, and on cooling crystals separate out, which have been separated by treatment with acetone. The insoluble part consists of dianthranol. From the solution, crystals are obtained which consist of yellow needles melting at 195—197° to a ruby-red liquid. This substance is soluble in benzene, xylene, chloroform, acetic acid, pyridine, amyl alcohol, or acetone, slightly so in methyl or ethyl alcohol, and insoluble in light petroleum. All these solutions have a colour ranging from yellow to red. It dissolves in strong sulphuric acid, forming an emerald-green solution from which water precipitates the substance unchanged. The substance has the composition $C_{27}H_{18}O$, and is supposed to be diphenylmethyleneanthraquinone,  $CPh_2{:}C{<}\begin{matrix}C_6H_4\\C_6H_4\end{matrix}{>}CO$. The molecular weight, determined by the boiling-point method, is normal in ethylene bromide, but the substance is polymerised in benzene and acetone. With benzene it yields a compound, $3C_{27}H_{18}O,2C_6H_6$. H. M. D.

The Fatty Esters of Cholesterol and Phytosterol, and the Anisotropic Liquid Phases of Cholesterol Derivatives.

FRANS M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, **9**, 78—88).—Cholesterol and phytosterol can be easily distinguished crystallographically if the solidification of the fused material is watched on a microscopic slide. The discrete crystals as they separate from a mixture of alcohol and ether are not, on the other hand, easy to distinguish.

A number of esters of cholesterol and phytosterol with the fatty acids were prepared, preferably by boiling the alcohol with the acid anhydride, and their melting points examined. Most of the cholesterol esters examined possessed two liquid phases, namely, an anisotropic and an isotropic liquid phase; with one exception, on the other hand, the phytosterol esters have only one liquid phase. The transition points of the various cholesterol esters have been determined, and a tabular list is given in the paper. The following esters were examined: cholesterol formate, acetate, propionate, butyrate, *iso*butyrate, valerate, *iso*valerate, hexoate, octoate, decoate, benzoate, phthalate, and stearate. The formation of the anisotropic liquid was frequently accompanied by a brilliant display of colours; in some cases, namely, the formate, the octoate, and the *iso*valerate, the anisotropic liquid phase appeared to be labile relatively to the isotropic phase, and could only be obtained by cooling the latter suddenly. Of the phytosterol esters, on the other hand, only the valerate is anomalous, two solid phases appearing to exist, which melt respectively at 67·1° and 30°; an anisotropic liquid phase appears also to exist.

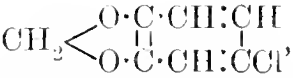
The melting points of mixtures of cholesterol and phytosterol, and of cholesterol and phytosterol acetates, have been reinvestigated: in both cases the melting point of the substance with the lower melting point, namely, the phytosterol or the cholesterol acetate, is raised by the other constituent of the mixture. K. J. P. O.

1 : 3-Dialkyl Ethers of Pyrogallol.

BASLER CHEMISCHE FABRIK (D.R.-P. 162658).—The trialkyl ethers of pyrogallol or of gallic esters are decomposed when heated with hydroxides of the alkalis or alkaline earths and water under pressure, yielding 1 : 3-dialkyl ethers of pyrogallol. Thus, the trialkyl gallates decompose according to the equation $C_6H_2(OR)_3{\cdot}CO_2R + 3NaOH = C_6H_2(OR)_2{\cdot}ONa + 2R{\cdot}OH + Na_2CO_3$.

Pyrogallol 1 : 3-*dimethyl ether* melts at 55—56° and boils at 258°. The *sodium* derivative forms large leaflets. *Pyrogallol* 1 : 3-*diethyl ether* crystallises from alcohol in long, colourless needles, melts at 79—80°, and boils at 263—265°. C. H. D.

Methylenecatechol and Certain of its Derivatives. EFISIO MAMELI (*Atti R. Accad. Lincei*, 1906, [v], **15**, ii, 101—108).—[With ENRICO BOI.]—Catechol methylene ether, obtained in small yield by Moureu (Abstr., 1897, i, 336) by the interaction of the sodium derivative of catechol and methylene iodide, can be prepared in larger quantity by reducing an alkaline solution of the diazo-chloride of *p*-aminocatechol methylene ether (this vol., i, 93) by means of stannous chloride. When treated with nitric acid of sp. gr. 1·40, catechol methylene ether yields *p*-nitrocatechol methylene ether (compare Jobst and Hesse, Abstr., 1878, 733; 1880, 325), whilst with acid of sp. gr. 1·44—1·52, dinitrocatechol methylene ether (Jobst and Hesse, *loc. cit.*) is obtained.

p-*Chlorocatechol methylene ether*,  $CH_2{<}\begin{array}{l}O\cdot C\cdot CH{:}CH\\ O\cdot C\cdot CH{:}CCl\end{array}$, prepared by the action of cuprous chloride on the diazochloride of *p*-aminocatechol methylene ether, is obtained as a colourless oil boiling at 185—187°. It reacts violently with concentrated nitric acid, giving a chloronitro-derivative melting at 128°.

p-*Bromocatechol methylene ether*, $CH_2O_2{:}C_6H_3Br$, is an oil which has a persistent, pungent odour, boils at 226—228°, dissolves readily in benzene, ether, or light petroleum, and to a less extent in alcohol, reacts energetically with concentrated nitric acid, and gives with concentrated sulphuric acid a carmine-red coloration which rapidly darkens.

p-*Iodocatechol methylene ether*, $CH_2O_2{:}C_6H_3I$, is obtained as a colourless oil, which boils at 156—157° under 30 mm. pressure and at 257—258° under the ordinary pressure. T. H. P.

Derivatives of Dicyanoquinol. JOHANNES THIELE and FRITZ GÜNTHER (*Annalen*, 1906, **349**, 45—66. Compare Abstr., 1900, i, 299).—When an alcoholic solution of chloroquinone and concentrated sulphuric acid is treated with a strong solution of potassium cyanide at the ordinary temperature, a good yield of dicyanoquinol is obtained. The *diacetate*, $C_{12}H_8O_4N_2$, forms white leaflets and melts at 165—166°; the *methyl* ether, $C_9H_6O_2N_2,H_2O$, separates from dilute alcohol in white needles and melts and decomposes at 225°, whilst its *acetate*, $C_{11}H_8O_3N_2$, melts at 136—137°. The dimethyl ether, $C_{10}H_8O_2N_2$, obtained in a sealed tube at 100° from sodium carbonate, methyl iodide, dicyanoquinol, and a little water, melts at 275°, and forms blue, fluorescent solutions in benzene or glacial acetic acid (compare Kauffmann, this vol., i, 287).

Dicyano-p-*benzoquinone*, $C_6H_2O_2(CN)_2$, is obtained by exposing a thin layer of dicyanoquinol in a desiccator to the vapour of concentrated nitric acid under slightly reduced pressure. After purification from chloroform solution, it forms orange-red prisms and melts at 175—180°. Boiling water causes an evolution of hydrogen cyanide and the formation of dicyanoquinol and viscous by-products.

2 : 3-*Dicyano*-6-*hydroxyquinol triacetate*, $C_{14}H_{10}O_6N_2$, is obtained by the prolonged action of concentrated sulphuric acid and acetic anhydride on dicyanoquinone. It separates from alcohol in white needles, melts at 160°, and is easily hydrolysed by dilute sulphuric acid to 2 : 3-*dicyano*-6-*hydroxyquinol*, $C_8H_4O_3N_2$, which decomposes at 250°, gives

a dark green coloration with ferric chloride, and dissolves in alkalis without fluorescence. *Chlorohydroxyquinol triacetate*, $C_6H_2Cl(OAc)_3$, prepared in a similar manner from chlorobenzoquinone, forms white needles and melts at 96—97°.

Chlorodicyanoquinol, $C_8H_3O_2N_2Cl$, prepared by passing hydrogen chloride into a solution or suspension of dicyanobenzoquinone in chloroform at 0°, forms white needles, melts and decomposes at 190°, develops a violet-red coloration with ferric chloride, and dissolves in sodium carbonate solution with a yellow fluorescence; the *diacetate* melts at 122—123°.

Chlorodicyanobenzoquinone, $C_8HO_2N_2Cl$, is obtained by oxidising the preceding quinol with the vapour of nitric acid in a desiccator. It separates from chloroform in yellow needles, melts at 154—155° to a dark red liquid, is decomposed by alkalis, and reduced by sulphurous acid. Hydrogen chloride converts it into *dichlorodicyanoquinol*, $C_8H_2O_2N_2Cl_2$, which decomposes at 265° and forms a *diacetate* melting at 181—182°.

Dichlorodicyanobenzoquinone, $C_8O_2N_2Cl_2$, forms golden leaflets, decomposes at 203°, liberates iodine from hydrogen iodide, and is reduced by sulphurous acid. Water decomposes it, producing a red coloration and evolving hydrogen cyanide.

Dibromodicyanoquinol, $C_8H_2O_2N_2Br_2$, obtained by heating dicyanoquinol in glacial acetic acid with bromine (2 mols.) and potassium acetate (2 mols.), forms yellow leaflets, gives a rose-red coloration with ferric chloride, decomposes at 250°, and cannot be hydrolysed to the corresponding phthalic acid. The *hydroxylamine* salt,

$$C_8H_2O_2N_2Br_2,2NH_2 \cdot OH,H_2O,$$

forms yellow needles, decomposes when heated, and is resolved into its components by boiling water. The *diacetate*, $C_{12}H_6O_4N_2Br_2$, melts at 199°.

By treatment with acetic anhydride and a few drops of concentrated sulphuric acid, Nef's benzoquinone dibromide (Abstr., 1890, 1272) is slowly changed into 2 : 5-dibromoquinol diacetate.

Dibromodicyanobenzoquinone, $C_8O_2N_2Br_2$, obtained by oxidising the corresponding quinol with the vapour of nitric acid, crystallises from chloroform in purple-red leaflets, decomposes at 210—217°, and liberates hydrogen cyanide on treatment with water.

The hydrolysis of dicyanoquinol by boiling potassium hydroxide solution gives *p*-dihydroxyphthalic acid, $C_8H_6O_6$, in good yield, which separates from water in greenish-yellow needles containing $\frac{1}{2}H_2O$ and melts at 213° with loss of water. The aqueous solution develops a deep violet coloration with ferric chloride; in alkaline solution a yellow fluorescence is observed. Bromine converts the acid into bromoanil, whilst heating with ammonium carbonate forms a *p*-dihydroxyphthalimide. The *anhydride*, $C_8H_4O_5$, obtained at 220—230°, separates from benzene in greenish-yellow nodules, which by exposure to air take up $1\frac{1}{2}H_2O$ and become sulphur-yellow. The *diacetate* of the anhydride, $C_{12}H_8O_7$, separates from benzene and light petroleum in white crystals and melts at 158°.

p-*Diacetoxyterephthalic acid*, $C_{12}H_{10}O_8$, forms white nodules and is stable at 260°. The *diacetate* of the ethyl ester melts at 156·5°.

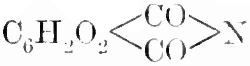
p-*Diacetoxyphthalimide*, $C_{12}H_9O_6N$, separates from alcohol in white needles, becomes yellow at 150°, and melts at 200°.

Dichloro-p-*dihydroxyphthalimide*, $C_8H_3O_4NCl_2$, obtained by heating dichlorodicyanoquinol with sulphuric acid and a trace of water, forms greenish-yellow crystals which change colour at 150° but do not melt at 270°.

Dibromo-p-*dihydroxyphthalimide*, $C_8H_3O_4NBr_2$, separates from alcohol as a yellow powder, melts and decomposes at 250°, gives a blue coloration with ferric chloride, and a yellow fluorescence in aqueous-alcoholic solution; the *diacetate* melts at 263°.

p-*Dimethoxyphthalimide*, obtained by hydrolysing dicyanoquinol dimethyl ether with concentrated sulphuric acid and a trace of water, forms yellow needles and decomposes at 200°.

p-*Dimethoxyphthalic anhydride*, $C_{10}H_8O_5$, obtained by boiling the preceding compound with alcoholic hydrogen chloride, forms greenish-yellow crystals, melts at 259°, and gives a blue fluorescence in alcoholic acetic acid.

Benzoquinonedicarboxylimide,  $C_6H_2O_2{<}\substack{CO\\CO}{>}NH$, obtained by oxidising *p*-dihydroxyphthalimide with the vapour of nitric acid, forms brick-red leaflets, decomposes at 220°, and is readily reduced by sulphurous acid. The *anhydride*, $C_8H_2O_5$, prepared in similar manner from *p*-dihydroxyphthalic anhydride, forms dark red leaflets. C. S.

Addition of Halogens and of Hydrogen Perhaloids to Oxygen Compounds. ARTHUR HANTZSCH and OSKAR DENSTORFF (*Annalen*, 1906, **349**, 1—44).—The yellow modification of α-diethoxydinaphthastilbene (Elbs, Abstr., 1893, i, 271) separates from a concentrated solution in a solvent of high boiling point, and the white form from a dilute solution; if the white needles are removed from the mother liquor, the remaining yellow plates change progressively into the labile modification. The chemical properties of the two modifications are identical, and they behave as physical isomerides. On the contrary, the white and yellow modifications of dibenzoylethylene (Paal, Abstr., 1902, i, 228) are geometrical isomerides, representing the *cis*- and the *trans*-forms respectively.

The additive compounds comprise two classes: (1) perhaloids, compounds of iodine or bromine with organic oxygen compounds, especially those containing an ethereal oxygen atom; (2) hydrogen perhaloids, compounds of HBr_n and HI_n with oxygen compounds, especially unsaturated ketones such as dibenzylideneacetone.

In the formation of these substances the nature of the solvent is of the utmost importance. The most suitable are associating solvents, such as benzene, carbon disulphide, and chloroform; dissociating solvents, such as alcohol, pyridine, acetone, or water, are unfavourable.

α-*Diethoxydinaphthastilbene tetra-iodide*,

$$OI_2Et\cdot C_{10}H_6\cdot CH{:}CH\cdot C_{10}H_6\cdot OI_2Et,$$

is instantaneously obtained as a dark, voluminous precipitate when a cold solution of diethoxydinaphthastilbene in carbon disulphide, benzene, or chloroform is treated with a large excess of a concentrated solution of iodine in the same solvent. In the dry state it is an amorphous, dark brown, compact powder, which melts and decomposes at 130—135°. By agitation with excess of carbon disulphide and of decinormal thiosulphate the iodine is removed quantitatively and the organic solvent acquires the pure yellow colour of diethoxydinaphthastilbene. In the freshly-precipitated state, the additive compound dissolves completely when rapidly heated with acetic acid, whereas a month-old preparation is only slightly soluble and decomposes by prolonged boiling.

a-Diethoxydinaphthastilbene dibromide tetra-iodide,

$OI_2Et{\cdot}C_{10}H_6{\cdot}CHBr{\cdot}CHBr{\cdot}C_{10}H_6{\cdot}OI_2Et$,

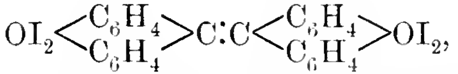
is obtained when the colourless dibromide is suspended in benzene and treated with a concentrated solution of iodine in the same solvent. When dry it is reddish-brown, and melts and decomposes at 146—152°.

a-Diethoxydinaphthastilbene dibromide perbromide,

$OEtBr_2{\cdot}C_{10}H_6{\cdot}CHBr{\cdot}CHBr{\cdot}C_{10}H_6{\cdot}OEtBr_2$ (?),

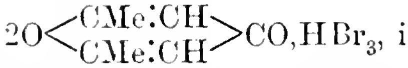
is prepared by treating the dibromide, suspended in carbon disulphide at − 75°, with a large excess of concentrated bromine solution. The black substance so obtained melts and decomposes at 80—95°, and loses bromine even when dried. Its composition is determined by analogy with the preceding tetraiodide. When the freshly-prepared substance is repeatedly shaken with carbon tetrachloride, glacial acetic acid, and light petroleum in succession, the added halogen is removed and the pure colourless dibromide is regenerated.

When finely-divided diethoxydinaphthastilbene is moistened with glacial acetic acid and treated with a dilute solution of bromine in the same solvent, it is instantly changed into a black *substance*, which, after being rapidly washed with alcohol and decomposed by alcoholic ammonia, regenerates the diethoxydinaphthastilbene. The substance is too unstable to be analysed, but is regarded as having the composition $OBr_2Et{\cdot}C_{10}H_6{\cdot}CH{:}CH{\cdot}C_{10}H_6{\cdot}OBr_2Et$; at low temperatures it loses bromine, yielding finally almost pure normal diethoxydinaphthastilbene dibromide.

Dixanthylene tetraiodide,  $OI_2{<}\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}{>}C{:}C{<}\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}{>}OI_2$, is a black substance which melts and decomposes at 135—140°; it is obtained as a microcrystalline powder by slow separation from the solution. The halogen is removed quantitatively by treatment with alcohol and sodium thiosulphate. In the presence of a large excess of iodine, the tetraiodide absorbs more halogen, yielding an octa- or a deca-iodide.

Dixanthylene tetrabromide is a brick-red, flocculent substance which melts and decomposes at 215—220°, and has its halogen removed quantitatively by aqueous-alcoholic sulphurous acid.

Hexane or light petroleum precipitates from a solution of iodine and dimethylpyrone in chloroform or carbon tetrachloride a yellowish-brown, viscous substance which cannot be isolated in a state suitable for analysis, but the existence of an additive compound of the two substances is indicated by the cryoscopic behaviour of their solution in ethylene dibromide, the observed depression being much smaller than the calculated value. The influence of the presence of various foreign substances has been studied, and the results, expressed graphically, serve to confirm the existence of an additive compound of iodine and dimethylpyrone.



Bisdimethylpyrone hydrogen tribromide, $2O{<}\substack{CMe:CH \\ CMe:CH}{>}CO,HBr_3$, is formed as an orange, flocculent precipitate on mixing solutions of dimethylpyrone and of bromine in wet ether. The substance is stable for a long time in a desiccator, separates from glacial acetic acid or chloroform in glistening, red needles, melts at 140—142°, and is insoluble in carbon disulphide, chloroform, or light petroleum. It is decolorised by alcoholic sulphurous acid or alcoholic ammonia, yielding dimethylpyrone.

Bisdibenzylideneacetone hydrogen pentaiodide, $2(CHPh:CH)_2CO,HI_5$, is obtained when the calculated quantity of hydrogen iodide, dissolved in benzene, is added to a dilute solution of the two components in an associating solvent. It is a voluminous, brownish-black substance, and melts and decomposes at 122—128°.

Bisdianisylideneacetone hydrogen pentaiodide,

$$2(OMe{\cdot}C_6H_4{\cdot}CH:CH)_2CO,HI_5,$$

obtained in a similar manner, is a greyish-black, amorphous substance which melts and decomposes at 137—142°.

Bisdianisylideneacetone hydrogen tri-iodide, $2C_{19}H_{18}O_3,HI_3$, exists in two modifications. One form is obtained by repeatedly extracting the preceding pentaiodide with warm ether, ethyl acetate, or glacial acetic acid until the residue consists of small, glistening, red prisms melting at 165—167°. When a solution of this form in boiling ethyl acetate or glacial acetic acid is cooled rapidly, the second modification is obtained in the form of dense, greenish-black needles, melting and decomposing at 156—159°. The latter, which in the mother liquor undergoes partial transformation into the first, can also be obtained by bringing together dianisylideneacetone and iodine in boiling glacial acetic acid or ethyl acetate. Both forms are converted into the pentaiodide by excess of iodine dissolved in benzene; alcohol, on the contrary, removes the halogen and regenerates dianisylideneacetone.

Bismonoanisylideneacetone hydrogen pentaiodide, $2C_{11}H_{12}O_2,HI_5$, separates slowly from a warm dilute solution of the ketone and iodine in carbon tetrachloride in the form of bluish-black, glistening leaflets, more quickly on addition of hydrogen iodide dissolved in benzene; it melts and decomposes at 116—122°. A pure hydrogen tri-iodide has not been obtained. At $-180°$ the colours of all these compounds become less intense.

In conformity with the theory that iodine dissolves to a brown solution in those solvents with which it can form additive compounds, the authors find that the intensely brown solution of dimethylpyrone periodide in ethylene dibromide becomes violet by dilution; also at a suitable concentration the brown solution of the same compound in carbon tetrachloride becomes violet by warming, and brown again by cooling.

Dinaphthastilbene and its dibromide do not form additive compounds. This is one of the several arguments advanced by the authors for regarding the halogen or hydrogen perhaloid in the preceding compounds as being united to oxygen by residual affinities. C. S.

Nitration of *p*-Acetylaminophenoxyacetic Acid, of Diacetyl-*p*-aminophenol, and of *p*-Acetanisidine. FRÉDÉRIC REVERDIN and ARTHUR BUCKY (*Arch. Sci. phys. nat.*, 1906, [iv], **22**, 124—145).—As with benzoyl- and dibenzoyl-*p*-aminophenol (Reverdin and Deletra, this vol., i, 165, 273), so also with *p*-acetylaminophenoxyacetic acid, nitration with a mixture of sulphuric and nitric acids yields products different from those obtained by using nitric acid alone (compare Howard, Abstr., 1898, i, 29).

2 : 5-*Dinitro-4-acetylaminophenoxyacetic acid*,

$$CO_2H\cdot CH_2\cdot O\cdot C_6H_2(NO_2)_2\cdot NHAc,$$

obtained by the action of sulphuric and nitric acids on *p*-acetylaminophenoxyacetic acid, crystallises in yellow to orange-yellow needles or plates melting at 176°, and dissolves readily in acetic acid, acetone, acetic anhydride, or solutions of the alkali hydroxides or carbonates, to a less extent in alcohol, and only sparingly in benzene or chloroform. Its *barium* salt ($+2H_2O$) crystallises in small, yellowish-brown prisms slightly soluble in cold water.

2 : 5-*Dinitro-4-aminophenoxyacetic acid*,

$$CO_2H\cdot CH_2\cdot O\cdot C_6H_2(NO_2)_2\cdot NH_2,$$

prepared by hydrolysing the acetyl derivative by means of concentrated sulphuric acid, crystallises from water in orange-red needles or plates, melts at 170°, and dissolves readily in alcohol, acetone, acetic acid, or solutions of the alkali hydroxides or carbonates. Its *barium* salt ($+3H_2O$) separates in brownish-red needles. Its *ethyl* ester crystallises in silky, red needles melting at 144°, and is soluble in acetic acid or benzene. When diazotised and treated with sulphuric acid and potassium iodide, the acid gives (1) an *iodo*-acid, which crystallises from light petroleum in faintly orange, yellow plates, melts at 114—115°, and dissolves in alcohol, benzene, acetic acid, chloroform, or dilute acetone; its *sodium* salt separates in slender, orange needles, its *potassium* salt in red crystals, and its *barium* salt in brown crystals; (2) another *iodo*-acid, crystallising from dilute acetic acid in yellow, flattened needles melting at 201—202°, and dissolving readily in acetone or alcohol and sparingly in benzene or chloroform; its *barium* salt forms yellowish-brown, prismatic needles.

Howard (*loc. cit.*) has assigned an erroneous structure to the acid obtained by the action of nitric acid alone on *p*-acetylaminophenoxyacetic acid, the authors' results showing that 2 : 3-dinitro-4-acetylaminophenoxyacetic acid is obtained under these conditions. The mother liquors from this acid are found to contain another acid, giving, on partial hydrolysis with concentrated sulphuric acid, 3 : 5-*dinitro-4-aminophenoxyacetic acid*, $C_8H_7O_7N_3$, which crystallises from water in long, red needles melting at 190°, and dissolves in alcohol or acetic acid, and to a slight extent in benzene; this acid is decomposed by alcohol, yielding a dinitrophenoxyacetic acid (?), which separates as a pale yellow, crystalline powder melting at 207°.

When diacetyl-*p*-aminophenol is nitrated by means of a mixture of sulphuric and nitric acids, the acetyl derivative of *iso*picramic acid, melting at 181°, is obtained. In this case, therefore, just as with dibenzoyl-*p*-aminophenol (Reverdin and Dresel, Abstr., 1905, i, 51), one of the acetyl groups first undergoes hydrolysis to hydroxyl. If, however, a mixture of sulphuric and nitric acids is added to a sulphuric acid solution of diacetyl-*p*-aminophenol containing acetic anhydride, a *compound*, $C_7H_6O_6N_3$, is obtained, which crystallises from dilute alcohol in golden-brown needles, decomposes at 163·5°, and dissolves in water or dilute acetic acid, and to a slight extent in benzene.

The nitroacetylanisidine [$OMe:NO_2:NHAc = 1:2:4$] of the Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 101778) crystallises from dilute acetic acid or aqueous alcohol in orange-yellow needles melting at 148—149°, and is soluble in water and slightly so in benzene or light petroleum. When *p*-acetylanisidine is nitrated by means of sulphuric and nitric acids it yields (1) the dinitro-*p*-acetylanisidine melting at 157° (Meldola and Stephens, Trans., 1905, **87**, 1199), and (2) a new *dinitro*-p-*acetylanisidine* [$OMe:(NO_2)_2:NHAc = 1:2:5:4$], which crystallises from dilute acetic acid in lemon-yellow crystals, melts at 175·5—176·5°, and dissolves readily in acetone, less so in alcohol, and sparingly in water, benzene, or light petroleum. Hydrolysis of the latter compound yields the corresponding *dinitro*-p-*anisidine* [$OMe:(NO_2)_2:NH_2 = 1:2:5:4$], which crystallises from a mixture of benzene and light petroleum in red needles melting at 153°, and is soluble in alcohol or acetic acid and readily so in benzene; it does not dissolve in a solution of sodium carbonate, or hydroxide, or ammonia, but gives a violet-red coloration which changes to yellow under the influence of heat.
T. H. P.

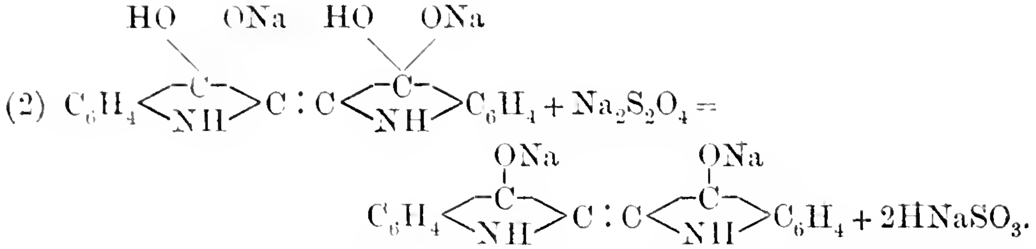
Preparation of Indoxyl and its Homologues. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 163039).—Compounds containing the group $-NR\cdot CH_2\cdot CO-$ (R = aryl), such as phenylglycine, phenylglycinephenylglycine, or their homologues, salts, esters, or amides, also phenylhydantoin and diphenylhydantoin, or their homologues, yield derivatives of indoxyl when heated with the alkali or alkaline earth metals or their alloys. The violence of the reaction is moderated by the addition of alkali hydroxides or cyanides.

Thus, potassium phenylglycine and an alloy of lead and sodium, added to a fused mixture of potassium and sodium hydroxides, give a product which yields 40—50 per cent. of indigotin on oxidation.
C. H. D.

Addition of Alkali to Indigotin. ARTHUR BINZ (*Zeit. angew. Chem.*, 1906, **19**, 1415—1418).—When powdered indigo is shaken for several days with alcoholic sodium hydroxide, a dark green powder is obtained which has the composition $C_{16}H_{10}O_2N_2,NaOH$; on exposure to the air, or on mixing with water, this substance turns blue with liberation of indigotin and sodium hydroxide; if the reaction is carried out at a temperature of 60° it is completed in a few minutes.

The corresponding compound, $C_{16}H_{10}O_2N_2,C_6H_5\cdot ONa$, which is obtained by heating powdered indigo for some minutes to 77° with alcoholic sodium phenoxide, is a dark green solid. It is assumed accordingly that the reactions taking place in the indigo vat may be represented as follows:

$$(1)\quad C_{16}H_{10}O_2N_2 + 2NaOH = C_{16}H_{10}O_2N_2,2NaOH.$$



$$(2)\ C_6H_4<\begin{matrix}\overset{HO\ \ ONa}{-C-}\\ NH\end{matrix}>C:C<\begin{matrix}\overset{HO\ \ ONa}{-C-}\\ NH\end{matrix}>C_6H_4 + Na_2S_2O_4 =$$

$$C_6H_4<\begin{matrix}\overset{ONa}{-C-}\\ NH\end{matrix}>C:C<\begin{matrix}\overset{ONa}{-C-}\\ NH\end{matrix}>C_6H_4 + 2HNaSO_3.$$

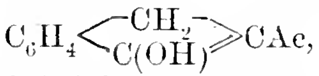
If equation (2) is correct, the reaction should be facilitated by the addition of alcohol, which diminishes hydrolysis. This was shown to be the case by experiment, in which it was found that the reaction took place about thirty times more quickly in alcoholic than in aqueous solution.

P. H.

Preparation of the Three Phthalaldehydes. JOHANNES THIELE and OSKAR GÜNTHER (*Annalen*, 1906, **347**, 106—111).—*o*-Phthalaldehyde is prepared by boiling ω-tetrabromo-*o*-xylene with potassium oxalate and dilute alcohol for forty hours until the whole has dissolved to a pale yellow solution, carbon monoxide and dioxide being evolved. After evaporating the solvent, the aldehyde is distilled in a current of steam and the distillate, after saturation with sodium sulphate, extracted with ethyl acetate. The pure aldehyde, crystallising in yellow needles melting at 56—56·5°, is obtained in a yield of 90 per cent.

[With LEOPOLD.]—*m*-Phthalaldehyde is prepared from *ω-tetrabromo-*m*-xylene*, $C_6H_4(CHBr_2)_2$, which crystallises in colourless needles melting at 107°. The tetrabromide is converted into corresponding aldehyde in a similar manner to the *o*-derivative; it is purified by conversion into the *trialdehydohydrobenzamide*, $(CHO{\cdot}C_6H_4{\cdot}CH)_3N_2$, which is a white, insoluble powder. The aldehyde crystallises in colourless needles melting at 89·5°; the dioxime melts at 180°. K. J. P. O.

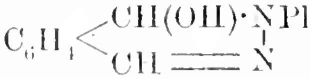
Condensation Products of *o*-Phthalaldehyde. JOHANNES THIELE and KAUFMAN G. FALK (*Annalen*, 1906, **347**, 112—131).—*2-Acetyl-3-hydrindone* (*2-acetyl-3-hydroxyindene*), $C_6H_4<\begin{matrix}CH_2\\ CO\end{matrix}>CHAc$ or



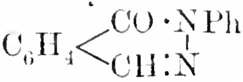
$$C_6H_4<\begin{matrix}-CH_2-\\ C(OH)\end{matrix}\geqslant CAc,$$

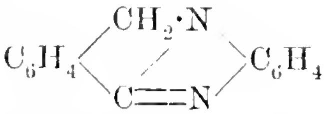
prepared by treating phthalaldehyde and acetone with potassium hydroxide, crystallises in pale yellow needles melting at 76·5°, and is readily soluble in alkali hydroxides; it yields a red coloration with ferric chloride in alcoholic solution, which becomes violet on addition of water. When bromine is added to its alkaline solution, 2:2-dibromohydrindone is obtained. The *phenylhydrazone* of acetylhydrindone crystallises in yellow, flattened needles or leaflets melting at 169—170°, and when treated with hydrochloric acid in methyl-alcoholic solution is converted into a *pyrazole* derivative, $C_{17}H_{14}N_2$, which crystallises in colourless prisms and melts at 84°.

Benzoylhydrindone (*2-benzoyl-3-hydroxyindene*), $C_6H_4<\begin{matrix}CH_2\\ CO\end{matrix}>CHBz$ or $C_6H_4<\begin{matrix}-CH_2-\\ C(OH)\end{matrix}\geqslant CBz$, is prepared in a similar manner from *o*-phthalaldehyde and acetophenone; it crystallises in yellow plates or pale yellow needles melting at 98·5°, and gives a deep green coloration with ferric chloride; by bromine it is converted into dibromohydrindone. Phenylhydrazine converts it into a corresponding *pyrazole*, $C_{22}H_{16}N_2$, which crystallises in red needles melting at 174°.

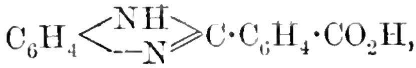
The *diphenylhydrazone* of *o*-phthalaldehyde, $C_6H_4(CH:N_2HPh)_2$, crystallises in golden-yellow needles melting at 190—191°. When boiled with dilute hydrochloric acid, it is converted into 1-*hydroxy*-2-*phenyl*-1 : 2-*dihydrophthalazine*,  $C_6H_4<\begin{array}{l}CH(OH)\cdot NPh\\ CH=\!=\!=N\end{array}$, which forms colourless crystals melting at 128—129°; its *methyl* ether is formed on merely dissolving the compound in methyl alcohol and forms white crystals melting at 59—60°; the *ethyl* ether melts at 96—97°; both ethers are reconverted into the original substance by dissolving them in acids and precipitating with an alkali.

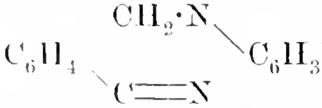
Phenylphthalazonium chloride,  $C_6H_4<\begin{array}{l}CH:NPhCl\\ CH:N\end{array}$, is prepared by passing dry hydrogen chloride into a solution of the hydroxydihydrophthalazine or one of its ethers in benzene; it crystallises in white needles melting at 106—107°, and is readily soluble in water. Its *aurichloride* crystallises in yellow needles melting at 181°; its *platinichloride* forms orange-red crystals melting at 224—225°.

Phenylphthalazone,  $C_6H_4<\begin{array}{l}CO\cdot NPh\\ CH:N\end{array}$, formed by oxidising the hydroxyphthalazine with alkaline permanganate, crystallises in needles melting at 106°, and is identical with the anhydride obtained by Racine (Abstr., 1887, 951) and Henriques (Abstr., 1888, 842) from phenylhydrazinephthalaldehydic acid.

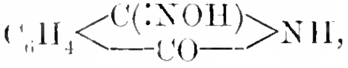
o-*Benzylenebenziminazole*,  $C_6H_4<\begin{array}{c}CH_2\cdot N\\ C=\!=N\end{array}>C_6H_4$, prepared by heating *o*-phthalaldehyde and *o*-phenylenediamine hydrochloride in aqueous solution and then precipitating the base with alkali, crystallises in needles melting at 210°, and yields a *hydrochloride* crystallising in needles; the *sulphate* crystallises in sparingly soluble leaflets; the *platinichloride* forms yellow crystals. When oxidised by permanganate in acid solution, a mixture of *benzoylenebenziminazole*,

$$C_6H_4<\begin{array}{c}CO\cdot N\\ C=N\end{array}>C_6H_4,$$

and phenylbenziminazole-*o*-carboxylic acid,  $C_6H_4<\begin{array}{c}NH\\ N\end{array}>C\cdot C_6H_4\cdot CO_2H$, is obtained; the former crystallises in yellow needles melting at 211—212°, and when boiled with alkalis or acids is rapidly hydrolysed to the latter, which melts at 273°. It is found to be identical with the "phthalyl-*o*-phenylenediamine" melting at 266°, prepared by Anderlini (Abstr., 1894, i, 375) from phthalic anhydride and *o*-phenylenediamine. The *ethyl* ester, $C_{16}H_{14}O_2N_2$, crystallising in leaflets melting at 163—164°, was obtained from the acid prepared by both methods. The *platinichloride*, $C_{32}H_{30}O_4N_4,PtCl_6$, obtained from the ester, is a yellow precipitate. When the acid is heated at 280—290°, or treated with acetic anhydride, it is reconverted into benzoylenebenziminazole.

o-Tolylenediamine and *o*-phthalaldehyde similarly yield *o-benzoylenetoliminazole*,  $C_6H_4<\begin{matrix}CH_2\cdot N\\ C{=\!=}N\end{matrix}>C_6H_3Me$, which forms colourless crystals melting at 192—193°; the *platinichloride* is a yellow precipitate.

The *compound* obtained by the action of hydroxylamine on *o*-phthalaldehyde is identical with the phthalimideoxime,



$$C_6H_4<\begin{matrix}C(:NOH)\\ CO\end{matrix}>NH,$$

prepared by Müller (Abstr., 1886, 802). K. J. P. O.

Thio-derivatives of Aromatic Aldehydes and Ketones and their Desulphurisation. Wilhelm Manchot and Chr. Zahn (*Annalen*, 1906, **345**, 315—334. Compare Abstr., 1905, i, 342).—*Dithiopiperonaldehyde*, $C_7H_5O_2\cdot CH_2\cdot S\cdot S\cdot CH_2\cdot C_7H_5O_2$, results after two to four weeks by the addition of finely-powdered piperonaldehyde to saturated alcoholic ammonium sulphide; it separates from alcohol and acetone in short, white prisms, melts at 69·5°, gives a carmine-red coloration with concentrated sulphuric acid, and is reduced by zinc dust and glacial acetic acid to the *mercaptan*, $C_8H_7O_2\cdot SH$, a yellow oil which forms yellow *lead* and *copper* salts, a greenish-yellow *silver* salt, and is reconverted into the disulphide by alcoholic iodine.

Dithiopiperonaldehyde hydrosulphide, $C_{16}H_{14}O_4S_2.H_2S$, results when alcoholic ammonium sulphide containing excess of hydrogen sulphide is used, and the mixture shaken for many days; it crystallises in slender needles, melts at 113°, does not form mercury or lead salts, is reduced to the mercaptan, and readily loses sulphur by treatment with a solution of sodium ethoxide or with copper powder.

Bis-3 : 4-*methylenedioxydibenzyl*, $C_{16}H_{14}O_4$, obtained from the disulphide and copper powder at 280° or by prolonged boiling in xylene, separates from alcohol in slender needles, melts at 138°, and yields a *bromide*, $C_{16}H_{12}O_4Br_2$, which melts at 164°.

Dithiovanillin, $C_{16}H_{18}O_4S_2$, obtained in a similar manner to the preceding disulphide, melts at 129—130°, loses sulphur by treatment with concentrated sulphuric acid or sodium hydroxide, and hydrogen sulphide by treatment with zinc dust and acetic acid; the *benzoyl* derivative, $C_{30}H_{26}O_6S_2$, melts at 133—135°, and does not form mercury or lead salts. *Dithiobromovanillin*, $C_{16}H_{16}O_4Br_2S_2$, prepared from Tiemann's bromovanillin, melts at 159°.

4 : 4′-*Dihydroxy*-3 : 3′-*dimethoxydibenzyl*, $C_{16}H_{18}O_4$, obtained from copper powder and dithiovanillin by heating alone or in xylene solution, forms long, slender needles, melts at 158°, produces a mirror with ammoniacal silver solutions, and yields a *bromide*, $C_{16}H_{14}O_4Br_4$, which melts at 214°.

Dithioanisaldehyde, $C_{16}H_{18}O_2S_2$, prepared previously in an impure state by Baumann and Fromm (Abstr., 1891, 1050), melts at 101°, and by careful heating with copper powder, alone or in xylene solution, yields p-*bismethoxydibenzyl*, $OMe\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot C_6H_4\cdot OMe$, which separates from alcohol in large needles, develops a magnificent red coloration with ferric chloride and concentrated sulphuric acid, and yields a *bromide*, $C_{16}H_{16}O_2Br_2$, which melts at 147°.

[By G. KRÄNZLEIN.]—*Dithio*-p-*dimethylaminobenzaldehyde*,

$$C_{18}H_{24}N_2S_2,$$

prepared like the preceding disulphides or by heating *p*-dimethylaminobenzaldehyde and ammonium sulphide at 100—120°, separates from alcohol in elongated prisms, melts at 83·5°, yields the *mercaptan* by reduction with sodium amalgam, and forms a *hydrochloride*,

$$C_{18}H_{24}N_2S_2,2HCl,$$

which melts at 211°. *Bis*-p-*dimethylaminodibenzyl*, $C_{18}H_{24}N_2$, boils at 105° under 25 mm. pressure, and forms a *platinichloride*,

$$C_{18}H_{24}N_2,H_2PtCl_6.$$

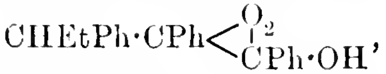
When *p*-dimethylaminobenzaldehyde is treated with alcoholic ammonium sulphide containing excess of hydrogen sulphide, a *hydrosulphide*, $C_{18}H_{24}N_2S_2,H_2S$, is obtained, which melts at 162°.

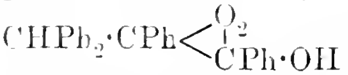
Bis-3 : 4-*methylenedioxystilbene*, $C_7H_5O_2{\cdot}CH{:}CH{\cdot}C_7H_5O_2$, obtained by heating α-trithiopiperonaldehyde (Wörner, Abstr., 1896, i, 225) and copper above 200°, separates from glacial acetic acid in short prisms and melts at 206°.
C. S.

Reaction between Unsaturated Compounds and Organic Magnesium Compounds. IX. Reactions with Stereoisomerides.

ELMER P. KOHLER (*Amer. Chem. J.*, 1906, **36**, 177—195. Compare this vol., i, 427; Kipping and Salway, Trans., 1904, **85**, 438).—The action of magnesium ethyl bromide on benzylidenedeoxybenzoin and *iso*benzylidenedeoxybenzoin, and treatment of the product with water or hydrochloric acid cooled with ice, leads to the formation of the two forms of αβ-diphenylvalerophenone, the relative amounts of the isomerides contained varying with the method of isolation. The action of benzoyl chloride on the magnesium compounds from the two isomerides results in the formation of the same *αβγ-triphenyl-Δ^α-pentenyl benzoate*, $CHEtPh{\cdot}CPh{:}CPh{\cdot}O{\cdot}COPh$, which crystallises from alcohol in long needles, melts at 143°, is not changed by heating at 150° for forty hours or by exposure to sunlight in benzene iodine solution, and on hydrolysis with aqueous potassium hydroxide cooled by ice or with concentrated hydrochloric acid at 150° yields the αβ-diphenylvalerophenone melting at 170°. The product obtained on hydrolysis of the benzoate with boiling alcoholic hydrogen chloride contains 10 per cent., or, with cold alcoholic hydrogen chloride, 14 per cent., of the isomeric ketone melting at 92°. The ketone melting at 92° is converted rapidly by potassium hydroxide, more slowly by hydrochloric acid, into its isomeride melting at 170°.

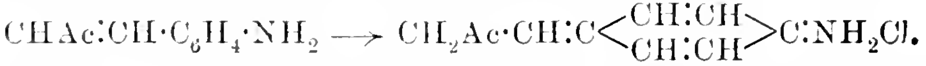
αβγ-Triphenyl-Δ^α-pentenyl acetate, $CHEtPh{\cdot}CPh{:}CPh{\cdot}OAc$, formed in a similar manner to the benzoate, crystallises in slender needles, melts at 120°, and on hydrolysis behaves in the same manner as the benzoate.

If the additive compound of magnesium ethyl bromide and benzylidene- or *iso*benzylidenedeoxybenzoin is poured on to ice and ether free from alcohol, it yields an oil which is probably *αβγ-triphenyl-Δ^α-pentenol*, $CHEtPh{\cdot}CPh{:}CPh{\cdot}OH$; this is readily soluble in cold light petroleum, reduces potassium permanganate in acetone solution, and in a freezing mixture changes slowly into *αβ*-diphenylvaleropheuone, of which 99·62 per cent. melts at 92° and 0·38 per cent. at 170°. When a current of air is passed through the moist ethereal solution of the enol cooled by a freezing mixture, the *peroxide*,  $\mathrm{CHEtPh{\cdot}CPh}<\begin{array}{l}\mathrm{O_2}\\ \mathrm{CPh{\cdot}OH}\end{array}$, is formed in two modifications, one of which crystallises from acetone in stout needles and melts at 166°; the other crystallises in large, transparent prisms and melts at 109°. These peroxides are not formed by the action of air or oxygen on *αβ*-diphenylvalerophenone; they are stable, do not yield hydrogen peroxide with water, do not liberate iodine from iodides, do not oxidise indigo, when heated in quantity decompose with a flash but without detonation, forming benzoic acid and ethyldeoxybenzoin, and react with magnesium ethyl bromide forming a *product* from which the peroxides are again formed on treatment with ice.

αβγγ-Tetraphenyl-Δ^α-propenol, $\mathrm{CHPh_2{\cdot}CPh{:}CPh{\cdot}OH}$, prepared by the action of magnesium phenyl bromide on benzylidenedeoxybenzoin in light petroleum solution, and treatment of the product with ice and ether free from alcohol, separates from light petroleum in colourless needles, melts at about 95—100°, and changes into triphenylpropiophenone when slowly heated below its melting point. The *peroxide*,  $\mathrm{CHPh_2{\cdot}CPh}<\begin{array}{l}\mathrm{O_2}\\ \mathrm{CPh{\cdot}OH}\end{array}$, crystallises in small, lustrous prisms, melts at 127°, and when heated alone, or with hydrochloric acid in alcoholic solution, decomposes, forming benzoic acid and diphenylacetophenone (Delacre, Abstr., 1896, i, 486; Biltz, Abstr., 1899, i, 439); this forms an *additive* compound with magnesium ethyl bromide, which reacts with water, yielding the *alcohol*, $\mathrm{CHPh_2{\cdot}CEtPh{\cdot}OH}$, crystallising in needles and melting at 91°. The *oxime* of diphenylacetophenone, $\mathrm{CHPh_2{\cdot}CPh{:}NOH}$, is obtained in small yields by the action of hydroxylamine hydrochloride on the ketone in aqueous potassium hydroxide solution. It crystallises from acetone in plates and melts at 182°.

Bromotriphenylpropiophenone, $\mathrm{CHPh_2{\cdot}CBrPh{\cdot}COPh}$, prepared by treating the magnesium derivative of tetraphenylpropenol with bromine, crystallises in large prisms, melts at 124°, and readily loses hydrogen bromide. G. Y.

Methinammonium Compounds. HANS RUPE and A. PORAI-KOSCHITZ (*Zeit. Farb. Ind.*, 1906, 5, 317—321).—The coloured salts of *p*-aminobenzylideneacetone are thought to be produced by a transition of the benzene nucleus into the quinonoid form, thus:



$$\mathrm{CHAc{:}CH{\cdot}C_6H_4{\cdot}NH_2} \longrightarrow \mathrm{CH_2Ac{\cdot}CH{:}C}<\begin{array}{c}\mathrm{CH{:}CH}\\ \mathrm{CH{:}CH}\end{array}>\mathrm{C{:}NH_2Cl}.$$

In order to test this hypothesis, it was necessary to investigate the *m* amino-compounds. Since the acetone derivatives are difficult to prepare, the corresponding acetophenone derivatives have been studied.

m-*Aminobenzylideneacetophenone*, $\mathrm{NO_2{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}COPh}$, prepared by reducing the corresponding nitro-derivative with stannous chloride in acetic acid solution, crystallises in pale yellowish green, rhombic leaflets melting at 159°; it dissolves in hydrochloric acid, forming a completely colourless solution, from which the *hydrochloride* can be isolated as colourless needles. The *sulphate* is similar. The *acetyl* derivative, prepared from the hydrochloride and acetic anhydride in the presence of sodium acetate, crystallises in yellow, prismatic needles melting at 104°.

p-*Aminobenzylideneacetophenone* crystallises in golden leaflets melting at 151°; it dissolves in moderately dilute hydrochloric acid, forming a deep red solution, which becomes decolorised by addition of concentrated hydrochloric acid, flesh-coloured needles finally separating. These crystals dissolve in hot concentrated hydrochloric acid with a red coloration, which, however, disappears on cooling. If water is cautiously added to the red solution, red crystals separate. Both forms have the same composition, $C_{15}H_{13}ON,HCl$. The solution of the base in acetic acid is deep red, and deposits dark red leaflets, which, on slowly heating, fade in colour, and finally melt at 151°, the melting point of the base. The *acetyl* derivative crystallises in pale green leaflets melting at 179°.

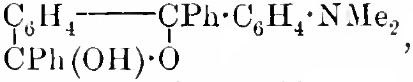
p-Aminoacetophenone and hydroxylamine yield two compounds according as sodium hydroxide or carbonate has been used to bring about the condensation. The simple *oxime*,

$$NH_2\cdot C_6H_4\cdot CH\colon CH\cdot CPh\colon NOH,$$

is formed in the presence of the hydroxide, and crystallises in leaflets melting at 139°. In presence of sodium carbonate, an *oximido-oxime*, $NH_2\cdot C_6H_4\cdot CH(NH\cdot OH)\cdot CH_2\cdot CPh\colon NOH$, is produced, and crystallises in needles melting at 178·5—179°; the *hydrochloride* is sparingly soluble.

p-Dimethylaminobenzylideneacetophenone forms a bluish-grey hydrochloride when treated with a small quantity of fuming hydrochloric acid; the solution in hydrochloric acid is blue. The base dissolves in dilute hot hydrochloric acid with a deep red coloration, which disappears on cooling, the solution depositing a colourless, crystalline *hydrochloride*, $C_{17}H_{17}ON,HCl$, crystallising in needles; this material again dissolves in hot acid with a red coloration. In concentrated sulphuric acid, the base forms a colourless solution, from which a small quantity of water precipitates a colourless sulphate. The solution in hot acid is red. The *phenylhydrazone* of *p*-dimethylaminobenzylideneacetophenone, $NMe_2\cdot C_6H_4\cdot CH\colon CH\cdot CPh\colon N\cdot NHPh$, forms very pale green needles melting at 127—128°. K. J. P. O.

Action of Magnesium Phenyl Bromide on Dialkylaminobenzoylbenzoic Esters. J. Pérard (*Compt. rend.*, 1906, **143**, 237—239).—2-*Hydroxy*-1-p-*dimethylaminophenyl*-1 : 2-*diphenyl*-1 : 2-*dihydroisobenzofuran*,



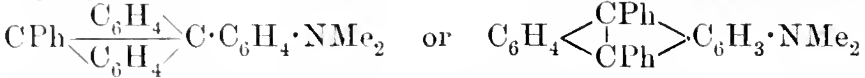
$$\begin{array}{l} C_6H_4 \text{———} CPh\cdot C_6H_4\cdot NMe_2 \\ | \qquad\qquad\quad | \\ CPh(OH)\cdot O \end{array}$$

, prepared by the action of excess of magnesium phenyl bromide on methyl dimethylaminobenzoylbenzoate (Haller and Guyot, Abstr., 1904, i, 602), crystallises from a mixture of benzene and alcohol in slender, faintly yellow needles melting at 194° (uncorr.), and dissolves in the hydrocarbons, to a less extent in the alcohols, and sparingly in ether or acetone. It is soluble in acids, forming intensely red salts, which crystallise from acetone in slender needles and are dissociated by water. The *picrate* melts and decomposes at 246°. The *methyl* and *ethyl* ethers crystallise from a mixture of benzene and alcohol in colourless prisms and melt at 158° and 169° respectively.

p-*Dimethylamino-o-benzhydryltriphenylcarbinol*,

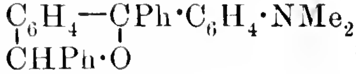
$$OH\cdot CHPh\cdot C_6H_4\cdot CPh(OH)\cdot C_6H_4\cdot NMe_2,$$

prepared by reducing the preceding compound by means of sodium amalgam and alcohol, separates from a mixture of alcohol and ether in white crystals and melts at 145°. Under the action of dehydrating agents, it is converted into (1) *dimethylaminodiphenylanthracene*,



$$CPh\begin{matrix}\diagup C_6H_4 \diagdown\\ \diagdown C_6H_4 \diagup\end{matrix}C\cdot C_6H_4\cdot NMe_2 \quad \text{or} \quad C_6H_4{<}\begin{matrix}CPh\\ |\\ CPh\end{matrix}{>}C_6H_3\cdot NMe_2$$

(compare Guyot and Catel, Abstr., 1905, i, 516), which separates from a mixture of benzene and light petroleum in microscopic, green crystals melting at 298°, and dissolves in acetic acid, carbon disulphide, or pyridine, and, to a slight extent, in alcohol; or (2) 1-p-*dimethylaminophenyl*-1:2-*diphenyl*-1:2-*dihydro*iso*benzofuran*,



$$\begin{array}{l}C_6H_4-CPh\cdot C_6H_4\cdot NMe_2\\ \;|\qquad\;\;|\\ CHPh\cdot O\end{array},$$

which crystallises from a mixture of benzene and alcohol in white prisms melting at 110°. T. H. P.

Introduction of Dinaphthapyryl and Xanthyl Radicles into Electro-negative Molecules. ROBERT FOSSE and A. ROBYN (*Compt. rend.*, 1906, **143**, 239—242).

—Dinaphthapyryl and xanthyl radicles can readily be substituted for a hydrogen atom of various electro-negative organic molecules, such as β-ketonic esters, β-diketones, or ethyl malonate or cyanoacetate, by: (1) the action of heat on a molecular mixture of xanthydrol with a β-ketonic or cyanoacetic ester; (2) contact in an acetic acid medium of either xanthydrol and a β-ketone or dinaphthapyranol and an acetoacetic ester; (3) double decomposition between dinaphthapyryl bromide and the sodium derivative of a β-ketonic ester, a β-diketone, or a malonic or cyanoacetic ester.

It has not been determined whether the union of the two constituent radicles of the compounds thus obtained is by means of carbon-carbon, carbon-oxygen, or oxygen-oxygen.

The following new compounds have been prepared:

Ethyl xanthylacetoacetate,

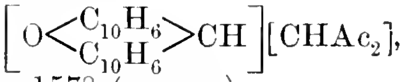
$$\left[O{<}\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}{>}CH\right][CHAc\cdot CO_2Et],$$

forms white, nacreous crystals and melts at 87—89°.

Ethyl xanthylethylacetoacetate, $[O(C_6H_4)_2CH][CEtAc\cdot CO_2Et]$, prepared by the action of sodium and ethyl iodide on the preceding compound, forms plates melting at 126—127°.

Ethyl xanthylbenzoylacetate, $[O(C_6H_4)_2CH][CHBz\cdot CO_2Et]$, forms groups of white needles melting at 80°.

Dinaphthapyrylacetylacetone,



$$\left[O{<}\begin{matrix}C_{10}H_6\\ C_{10}H_6\end{matrix}{>}CH\right][CHAc_2],$$

forms colourless crystals melting at 155—157° (uncorr.).

Xanthylacetylacetone, $[O(C_6H_4)_2CH][CHAc_2]$, crystallises in long, white needles melting at 141—142° (uncorr.).

Dinaphthapyrylbenzoylacetone, $[O(C_{10}H_6)_2CH][CHAcBz]$, forms colourless crystals melting and decomposing at about 201—204°.

Xanthylbenzoylacetone, $[O(C_6H_4)_2CH][CHAcBz]$, forms white crystals melting at 171° (uncorr.).

Ethyl dinaphthapyrylmalonate, $[O(C_{10}H_6)_2CH][CH(CO_2Et)_2]$, forms large, colourless crystals melting at 109—110°.

Ethyl dinaphthapyrylcyanoacetate, $[O(C_{10}H_6)_2CH][CN\cdot CH\cdot CO_2Et]$, melts at 158—159° (uncorr.).

Ethyl xanthylcyanoacetate, $[O(C_6H_4)_2CH][CN\cdot CH\cdot CO_2Et]$, forms pale green crystals melting at 124—126° (uncorr.). T. H. P.

Grignard's Reaction. RICHARD MEYER and KARL TÖGEL (*Annalen*, 1906, **347**, 55—92).—The use of Grignard's reaction in the synthesis of benzoic acid has been studied (compare Houben and Kesselkaul, Abstr., 1902, i, 583; and Zelinsky, *ibid.*, 675). The action of carbon dioxide on magnesium phenyl bromide was mainly used, a trace of iodine being added as an accelerator. The influence of moisture and of temperature on the products of the reaction were studied in detail.

When magnesium is added to an ethereal solution of bromobenzene and carbon dioxide slowly passed in, benzoic acid is produced in nearly a theoretical yield, if the presence of moisture is most carefully avoided. At the same time a trace of diphenyl is always formed.

In the presence of even an extremely small quantity of water the yield of benzoic acid falls to 25 per cent., whilst that of the diphenyl rises to about 65 per cent.

If the water is introduced not at the beginning but towards the end of the reaction, a third product, benzene, is formed at the expense of the benzoic acid and the diphenyl. The percentage of benzene is in the most favourable circumstances 64, whereas that of the benzoic acid is now 20, and that of the diphenyl 45.

At temperatures above 0° other products are formed; of these the chief is triphenylcarbinol, an oil being produced at the same time from which, on fractionation under reduced pressure, benzophenone and triphenylmethane can be isolated in small quantity together with diphenyl- and triphenyl-carbinols (compare Schroeter, Abstr., 1903, i, 821). In all the reactions above mentioned a trace of phenol is formed.

It is suggested that the following series of reactions takes place. In the absence of water the main reaction is represented by the equations: $C_6H_5Br + Mg = C_6H_5\cdot MgBr$; $C_6H_5\cdot MgBr + CO_2 = C_6H_5\cdot CO_2\cdot MgBr$. The diphenyl is formed probably according to the equation: $2C_6H_5Br + Mg = C_6H_5\cdot C_6H_5 + MgBr_2$, but it is probably also produced as the result of other changes in which phenol is the first product: $C_6H_5\cdot MgBr + H_2O + O = C_6H_5\cdot OH + MgBr\cdot OH$; $C_6H_5\cdot MgBr + C_6H_5\cdot OH = C_6H_5\cdot C_6H_5 + MgBr\cdot OH$. Hence only traces of phenol can be detected. In a special experiment, in which freshly-prepared magnesium phenyl bromide was treated with one mol. of phenol, rather more than one mol. of diphenyl was formed; prepared in this way, however, this substance could not be purified readily.

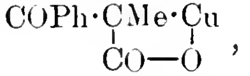
The benzene is most probably the result of the simple action of water on magnesium phenyl bromide: $C_6H_5\cdot MgBr + H_2O = C_6H_6 + MgBr\cdot OH$, a result which was tested by treating magnesium phenyl bromide with carbon dioxide in the presence of varying quantities of water. The benzophenone results from the interaction of one mol. of carbon dioxide with two mols. of magnesium phenyl bromide and subsequent decomposition of the additive product with water. The triphenylcarbinol is probably not produced directly from carbon dioxide and magnesium phenyl bromide, but from benzophenone, thus: $COPh_2 + C_6H_5\cdot MgBr = CPh_3\cdot O\cdot MgBr \longrightarrow CPh_3\cdot OH$, in harmony with the production of tertiary alcohols from ketones by Grignard's reaction. The triphenylmethane is probably a reduction product of the forerunner of the triphenylcarbinol.

Synthesis of the Esters of Ketonic Acids.—Unsuccessful attempts have been made to synthesise the esters of ketonic acids by the action of magnesium on a mixture of molecular proportions of an acyl chloride and halogenated ester. A magnesium-gold couple and a mercury-aluminium couple were also tried and found to be useless; but Grignard's reagent in the presence of a trace of aluminium can be used successfully if the right concentrations of ether are chosen. It is of importance to allow the magnesium to interact first with the halogenated ester.

Ethyl benzoylacetate is prepared by adding magnesium ribbon to a solution of ethyl bromoacetate in ether containing a trace of iodine. A vigorous reaction takes place as the magnesium dissolves and a thick oil separates; benzoyl bromide is now added in small portions and the mixture heated. The ethyl benzoylacetate is then converted into the sodium derivative and after acidification extracted with ether.

Benzoylacetic acid is obtained from the ester by hydrolysing by Ceresole's method; the acid melts and decomposes at 100—101°. Ethyl benzoylacetate was also prepared, but with a less satisfactory yield, from ethyl chloroacetate and benzoyl chloride in the presence of aluminium and magnesium.

Ethyl α-benzoylpropionate, similarly prepared from ethyl α-bromopropionate and benzoyl bromide, boils at 100—102° under 48 mm. pressure. The *copper* salt is a green powder decomposing at 180° and readily soluble in organic solvents. If the ester is treated with copper acetate in the presence of an alkali hydroxide, the *copper* salt,



$$\begin{array}{l} COPh\cdot CMe\cdot Cu \\ \qquad\quad | \qquad\; | \\ \qquad\; CO—O \end{array},$$

is produced. Attempts to obtain α-dibenzoylpropionic acid and tribenzoylacetic acid led to no results. When ethyl α-benzoylpropionate is hydrolysed, only benzoic and propionic acids are isolated.

Ethyl β-benzoylpropionate, obtained by the method above described from ethyl β-iodopropionate and benzoyl bromide, crystallises in leaflets, melts at 19°, and boils at 183—184° under 22 mm. pressure. When hydrolysed with barium hydroxide, the *barium* salt,

$$(CH_2Bz\cdot CH_2\cdot CO_2)_2Ba,$$

is obtained and crystallises in small needles. From the latter, the acid can be easily prepared. β-Dibenzoylpropionic acid, obtained by the action of benzoyl chloride on ethyl β-benzoylpropionate in the presence of sodium ethoxide, melts at 194° and gives a red coloration with ferric chloride.

Ethyl acetoacetate is prepared from ethyl bromoacetate and acetyl chloride.

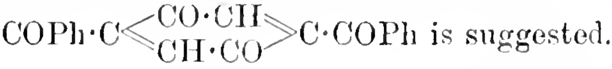
Attempts to condense ethyl *m*-bromobenzoate with benzoyl bromide failed. K. J. P. O.

Pechmann's Dye [from Benzoylacrylic Acid]. I. TAD. KÓZNIEWSKI and LEON MARCHLEWSKI (*Bull. Acad. Sci. Cracow*, 1906, 81—95).—Homologues of benzoylacrylic acid have been prepared by condensing aromatic hydrocarbons with maleic anhydride in the presence of aluminium chloride. The *phenylhydrazone* of benzoylacrylic acid, $C_{16}H_{14}O_2N_2$, crystallises from benzene in golden-yellow needles and melts at 197°. The *methyl ester* of the acid, $COPh{\cdot}CH{:}CH{\cdot}CO_2Me$, forms pale yellow needles melting at 30—32°, and boiling at 185° under 16 mm. pressure.

m-*Xyloylacrylic acid*, $C_6H_3Me_2{\cdot}CO{\cdot}CH{:}CH{\cdot}CO_2H$, is best prepared at low temperatures, and melts at 114°. *Phenetoylacrylic acid*, $OEt{\cdot}C_6H_4{\cdot}CO{\cdot}CH{:}CH{\cdot}CO_2H$, melts at 143—144°; *ψ-cumoylacrylic acid*, $C_6H_2Me_3{\cdot}CO{\cdot}CH{:}CH{\cdot}CO_2H$, melts at 149°, and the isomeric *mesitoylacrylic acid* at 140·5°.

Each acid yields a dye corresponding with Pechmann's dye from benzoylacrylic acid (Abstr., 1882, 1074) when warmed with dehydrating agents, especially acetic anhydride. The yields in most cases are poor. A better yield of dye appears to be formed when the benzoylacrylic acid contains γ-keto-α-hydroxyphenylbutyric acid, due to admixture of malic anhydride with the maleic anhydride. The dye from mesitoylacrylic acid is more readily soluble in chloroform or xylene than its homologues, and its solutions are coloured reddish-yellow, and possess a somewhat different absorption spectrum.

When oxidised, the dye from benzoylacrylic acid yields benzoic, and that from toluylacrylic acid, terephthalic acid. The dye from benzoylacrylic acid reacts with aniline and acetic acid, yielding a *dianilide*, $C_{32}H_{22}O_2N_2$, which crystallises in dark green, glistening needles soluble in xylene to a deep purple solution. Both alcoholic potassium hydroxide and bromine react with Pechmann's dye, for which the formula



$$COPh{\cdot}C\genfrac{}{}{0pt}{}{\diagup CO{\cdot}CH \diagdown}{\diagdown CH{\cdot}CO \diagup}C{\cdot}COPh$$

is suggested. J. J. S.

Hippocoprosterol. GERSON GITTELMACHER-WILENKO (*Bull. Acad. Sci. Cracow*, 1906, 20—23).—Bondzyński and Humnicki's hippocoprosterol (Abstr., 1897, i, 183) consists of two compounds.

α-Hippocoprosterol, $C_{27}H_{54}O$ or $C_{27}H_{52}O$, dissolves readily in 97 per cent. alcohol, crystallises in slender, rhombic plates resembling cholesterol, and melts at 66—67°. It gives Salkowski's and Liebermann's reactions but feebly.

β-Hippocoprosterol, $C_{27}H_{52}O$ or $C_{27}H_{50}O$, is almost insoluble in cold alcohol, separates as a gelatinous mass of minute needles, and melts at 56°. J. J. S.

β-Nitro*iso*apioles. ENRICO RIMINI and F. OLIVARI (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 138—141).—Dill *isoapiole nitrosite*, $C_{12}H_{14}O_7N_2$, prepared by a method analogous to that used for obtaining *iso*myristicin nitrosite (compare Rimini, Abstr., 1905, i, 656), is a lemon-yellow powder melting and decomposing at about 134°. The corresponding *β-nitroisoapiole*, $C_{12}H_{13}O_6N$, separates from alcohol in yellow crystals and melts at 94—95°.

The isomeric *β-nitroisoapiole*, obtained from parsley oil, crystallises from alcohol in silky, yellow needles melting at 96°. The *bromo-derivative*, $C_6Br(O_2CH_2)(OMe)_2 \cdot CH \colon CMe \cdot NO_2$, crystallises from alcohol in yellow laminæ melting at 120°. On treatment with hydroxylamine (1 mol.), this β-nitro*iso*apiole, in aqueous-alcoholic solution, gives *apiolaldoxime*, $C_{11}H_{10}O_5N$, melting at 160°.

In the preparation of β-nitro*iso*myristicin (*loc. cit.*), myristicinaldehyde is also formed, and in that of β-nitro*iso*apiole from parsley oil, apiolaldehyde is obtained in small quantity. T. H. P.

Bixin. The Colouring Matter of Bixa Orleana. I. LEON MARCHLEWSKI and LAD. MATEJKO (*Bull. Acad. Sci. Cracow*, 1905, 745—753. Compare Etti, *Ber.*, 1878, **11**, 864; Zwick, Abstr., 1897, i, 630).—Bixin crystallises from a mixture of chloroform and alcohol or from glacial acetic acid in dark red rhomboids melting at 198° when heated quickly, or at 191·5° when slowly heated. Its solubility in chloroform at 25° is 0·34 gram per 100. The analyses agree with Etti's formula, $C_{28}H_{34}O_5$. Its spectra in chloroform and alcoholic solutions are similar to those of lipochrom (*Proc. Roy. Soc.*, 1898, **63**, 389; 1899, **65**, 177). Monosodium and potassium salts have been prepared. Bixin contains one methoxyl group, and although it possesses distinct acidic properties, definite alkyl derivatives could not be prepared. When reduced with zinc dust and acetic acid, bixin yields an orange product melting at 200·5°. It rapidly changes when exposed to the air at 100° and becomes colourless. J. J. S.

Tannins. II. Eutannin. HERMANN THOMS (*Chem. Centr.*, 1906, i, 1829—1830; from *Apoth.-Zeit.*, **21**, 354—356. Compare this vol., ii, 504).—Commercial eutannin, free from lactose, is found to be identical with chebulinic acid, $C_{28}H_{22}O_{19}$. It crystallises from water in small, colourless needles containing H_2O and decomposing at 234°, and dissolves readily in alcohol, acetone, ethyl acetate, or amyl alcohol, sparingly in chloroform or light petroleum. It reacts acid towards litmus and has $[\alpha]_D$ initially $+61·7°$, gradually rising to $+66·9°$. It forms an *ennea-acetyl* derivative and a *methyl* derivative, the latter yielding trimethylgallic acid when treated with concentrated sodium hydroxide solution. When heated with water at 100—150°, eutannin yields gallic acid and *eutannin hydrate*, $C_{28}H_{24}O_{20}$, which is a white, amorphous powder decomposing at 200—210°; it dissolves readily in water, alcohol, acetone, or ethyl acetate and moderately in ether.

On dissolving eutannin in cold dilute sodium hydroxide solution in absence of air and subsequently acidifying with acetic acid and adding lead acetate solution, a precipitate is formed which, when treated with hydrogen sulphide, yields gallic acid and a *decomposition-tannin*, $C_{14}H_{16}O_{12}$ or $C_{14}H_{14}O_{11}$, as a pale yellow, amorphous powder, soluble in water, alcohol, acetone, ethyl acetate, or ether; it decomposes at about 260°, has $[\alpha]_D + 26°$ at 15°, gives a blue coloration with ferric chloride, reduces Fehling's solution slightly, has an acid reaction towards litmus, and yields a white precipitate with quinine salts.

Probable formulæ are suggested for the above compounds.

T. H. P.

Quebracho Tannin. II. Maximilian Nierenstein (*Chem. Centr.*, 1906, i, 1893; from *Collegium*, 1906, 141—142. Compare this vol., i, 446).—One gram of quebracho-tannin, either alone or with 100 grams of sodium acetate (compare Perkin and Yoshitake, Trans., 1902, **81**, 1164), is dissolved in 500 c.c. of water, and to the well-cooled solution 0·5 per cent. diazobenzene chloride solution is added, drop by drop, until a permanent turbidity appears. After twenty-four hours, the deposit formed is repeatedly extracted with boiling acetone. An amorphous product is thus obtained which melts above 360°, is insoluble in alcohol and other solvents, and gives, on analysis, the numbers: (1) C, 52·2; H, 3·18; and N, 14·55 per cent., when prepared without sodium acetate; and (2) C, 52·55, 54·40, and 59·90; H, 2·97, 3·18, and 4·00; N, 13·17, 14·50, and 14·55 per cent., when prepared by Perkin and Yoshitake's method. On boiling the azo-compound for forty hours with absolute alcohol and evaporating, there remains an amorphous, red, optically inactive residue, which dissolves in water or alcohol, gives all the reactions of a catechol-tannin, and contains 56·6 per cent. of carbon and 3·2 of hydrogen. This result tends to confirm the author's view (Abstr., 1905, i, 914) that the activity of the colouring matter may depend on the sugar which accompanies it. T. H. P.

Derivatives of Dihydro*iso*benzofuran. Parts I to III. Alfred Guyot and J. Catel (*Bull. Soc. chim.*, 1906, [iii], **35**, 551—562, 562—567, 567—571).—Most of the facts recorded in these papers have been published previously (Abstr., 1905, i, 226, 516, 540). 2-Hydroxy-1 : 1 : 2-triphenyl-1 : 2-dihydro*iso*benzofuran (Abstr., 1905, i, 226) separates from carbon disulphide in splendid crystals belonging to the monoclinic system, and is soluble in most organic solvents. *o*-Benzhydryltriphenylcarbinol (*loc. cit.*), produced by reducing the foregoing with sodium amalgam, when warmed in acetic acid solution with hydrochloric acid gives 1 : 1 : 2-*triphenyl*-1 : 2-*dihydro*iso*benzofuran*,

$C_6H_4\lt\begin{matrix}CPh_2-\\CHPh\end{matrix}\gt O$, which crystallises from boiling alcohol in leaflets and melts at 120°. On oxidation with chromic acid, it is re-converted into the parent hydroxytriphenyl*iso*benzofuran, and, like the latter, yields 9 : 10-diphenylanthracene when heated with sulphuric acid.

1 : 1-Diphenyl-1 : 2-dihydro*iso*benzofuran (Abstr., 1905, i, 517) separates from organic solvents in colourless leaflets and melts at 93°.

T. A. H.

Constitution of Hordenine. Eugène Léger (*Compt. rend.*, 1906, **143**, 234—236. Compare this vol., i, 204).—The oxidation of hordenine by either alkaline or acid potassium permanganate or chromic acid yields only oxalic acid, whilst, when nitric acid is employed, picric acid is also obtained.

Hordenine methiodide, when treated with silver hydroxide, yields the methoxide, which, on distillation in an oil-bath, gives trimethylamine; a dense, colourless oil, having an agreeable aromatic odour and volatile in a current of steam; and an amorphous, phenolic compound non-volatile at 180—190°.

On the basis of these results, the author suggests the formula $OH\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot NMe_2$ for hordenine. T. H. P.

Meroquinenine and the Constitution of the Cinchona Alkaloids. Wilhelm Koenigs (*Annalen*, 1906, **347**, 143—232).—The introduction to this paper contains a complete historical account of the investigations on the alkaloids of the cinchona bark. The researches which bear on the constitution of these alkaloids are discussed at length.

[With Karl Bernhart and Josef Ibele.]—Of the methods of preparing meroquinenine, namely, the hydrolysis of cinchenine with phosphoric acid, the hydrolysis of quinine, and the oxidation of cinchonine with chromic acid, the last mentioned is the most effective.

Pure meroquinenine melts and decomposes at 223—224° and has $[\alpha]_D = 27\cdot58—27\cdot9°$ at 20° in a 10 per cent. aqueous solution (compare Abstr., 1894, i, 477). The *hydrochloride* forms colourless crystals melting at 146—148°, and the *aurichloride*, yellow needles which melt and decompose at 142°. The *monomethyl ether*, $C_9H_{14}O_2NMe$, prepared from the alkaloid and methyl alcohol in the presence of sulphuric acid, is a colourless oil which yields a crystalline *hydrochloride*; the *hydrochloride* of the *ethyl ether* crystallises in needles melting at 165°.

Meroquinenine yields an *acetyl* derivative, $C_9H_{14}O_2NAc$, which crystallises in plates melting at 110°; it still possesses faint basic properties, but at the same time has marked acid properties and yields a *silver* salt. The *ethyl* ester of the acetyl derivative is an oil.

Nitrosomeroquinenine, $C_9H_{14}O_2N\cdot NO$, prepared from the alkaloid and sodium nitrite in the presence of dilute sulphuric acid, forms colourless crystals melting at 67°; its *calcium* salt,

$$(C_9H_{13}O_3N_2)_2Ca,2H_2O,$$

by means of which it is purified, is a soluble crystalline powder. The markedly acid properties of the acetyl and nitroso-derivatives show the presence of a carboxyl group, which is masked in the original alkaloid by the amino-group.

When meroquinenine is oxidised by a mixture of chromic and sulphuric acids, cincholeuponic acid is mainly formed, together with formic acid. When reduced with fuming hydriodic acid, meroquinenine is converted into cincholeupone, $C_9H_{17}O_2N$.

When meroquinenine is vigorously reduced with hydriodic acid and red phosphorus, 2-methyl-3-ethylpyridine is formed; the *picrate* crystallises in needles melting at 148—150°, and the *aurichloride* in yellow needles melting at 138°; when oxidised with permanganate, a mixture of 3:4-pyridinedicarboxylic and 4-methylpyridine-3-carboxylic acids is produced, the constitution of the pyridine being thus demonstrated.

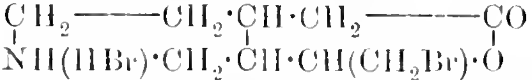
On treating meroquinenine with bromine water, a compound,

$$C_9H_{14}O_2NBr,HBr,$$

is formed, which can be reduced by zinc dust and sulphuric acid to meroquinenine. This *hydrobromide* yields a nitroso-derivative,

$$C_9H_{13}O_2NBr\cdot NO,$$

forming colourless crystals melting at 98° (compare Koenigs and Comstock, Abstr., 1884, 1382), which has, however, no acid properties, and is probably represented by the formula

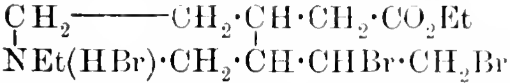


$$\begin{array}{l}CH_2\text{———}CH_2\cdot CH\cdot CH_2\text{———}CO\\ NH(HBr)\cdot CH_2\cdot CH\cdot CH(CH_2Br)\cdot O\end{array};$$

in the action of the bromine water, the halogen is first of all added to the ethylene linking, and then one bromine atom eliminated with the hydrogen of the carboxyl group, a lactone ring being formed.

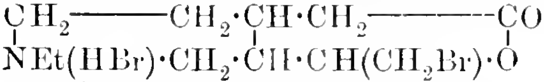
Hydroxymeroquinenine, $C_9H_{14}O_2N\cdot OH$, is obtained as a hydrochloride by boiling the hydrobromide just described with an aqueous suspension of silver chloride; it crystallises with H_2O and melts and decomposes at 254°; the *hydrochloride* crystallises in needles melting and decomposing at 208—210°, and yields a *platinichloride* decomposing at 240°; the *aurichloride* crystallises in needles, melting and decomposing at 184°. A *monoacetyl* derivative was obtained by heating the hydroxy-compound with acetic anhydride and isolated as an *aurichloride*, $C_{11}H_{17}O_4N,HAuCl_4$, which melts and decomposes at 214°. Attempts to esterify hydroxymeroquinenine were unsuccessful.

When the ethyl ester of meroquinenine is treated with ethyl iodide, the *ethyl* ester of N-*ethylmeroquinenine hydriodide*, $C_9H_{13}NEtO_2Et,HI$, is obtained as colourless needles melting at 156—157°; by treatment with silver chloride it can be converted into the corresponding *hydrochloride*, which crystallises in colourless prisms melting at 220—221°; the corresponding *hydrobromide* melts at 194°. When boiled with aqueous hydrochloric acid, these esters are hydrolysed and the *hydrochloride* of *N*-ethylmeroquinenine, $C_{11}H_{19}O_2N,HCl$, which melts at 165°, is produced. The base could not be obtained in a crystalline form. When the hydrobromide of the ethyl ester of *N*-ethylmeroquinenine is treated with bromine in chloroform solution, two atoms of bromine are added on at the ethylene linking, and the compound



$$\begin{array}{l}CH_2\text{———}CH_2\cdot CH\cdot CH_2\cdot CO_2Et\\ NEt(HBr)\cdot CH_2\cdot CH\cdot CHBr\cdot CH_2Br\end{array}$$

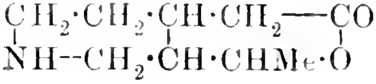
is produced; it crystallises in colourless needles, melting and decomposing at 182°. When hydrolysed by boiling dilute hydrobromic acid, the *hydrobromide* of N-*ethylbromomeroquinenine*,



$$\begin{array}{l}CH_2\text{———}CH_2\cdot CH\cdot CH_2\text{———}CO\\ NEt(HBr)\cdot CH_2\cdot CH\cdot CH(CH_2Br)\cdot O\end{array},$$

is formed, a lactone ring at the same time appearing; it crystallises in colourless needles melting and decomposing at 218—220°.

When meroquinenine is heated with a concentrated solution of arsenic acid at 180—190°, oxidation does not occur, but the elements of water are added, a hydroxydihydromeroquinenine being formed; when treated with hydrochloric acid, water is again eliminated, a *hydrochloride* melting and decomposing at 255—256° being produced, which is isomeric with the hydrochloride of meroquinenine. From this hydrochloride, the base, *meroquinenine lactone*,



$$\begin{array}{l}CH_2\cdot CH_2\cdot CH\cdot CH_2\text{—}CO\\ NH\text{—}CH_2\cdot CH\cdot CHMe\cdot O\end{array},2H_2O,$$

or *hydroxydihydromeroquinenine*, can be prepared, and crystallises in colourless prisms melting and decomposing at 220°. When the hydrochloride is treated with bromine or iodine and sodium hydroxide, bromoform and iodoform are respectively produced, reactions which indicate the presence of a methyl group as in the above formula.

On heating meroquinenine with hydrochloric acid, a meroquinenine lactone is not produced in any quantity, but the major portion of the base is converted into a lævorotatory base, the *platinichloride* of which crystallises in yellow needles or leaflets melting and decomposing at 232°. K. J. P. O.

The Relations between Functional (Reactive) Groups in Remote Positions. Decamethyleneimine.

EDMOND E. BLAISE and L. HOUILLON (*Compt. rend.*, 1906, **143**, 361—363. Compare this vol., i, 692).—By the action of heat on decamethylenediamine hydrochloride, a mixture of bases is obtained which contains a small quantity of 2-*hexylpyrrolidine*; the *platinichloride*, *aurichloride*, and *carbamide* of this base melt at 117°, 85°, and 146° respectively, and are identical with the corresponding derivatives of 2-hexylpyrrolidine prepared synthetically by a similar method to that adopted in the synthesis of 2-butylpyrrolidine (*loc. cit.*).

ι-Aminodecoic acid, $CO_2H\cdot[CH_2]_8\cdot CH_2\cdot NH_2$, prepared from brassylamic acid, $CO_2H\cdot[CH_2]_9\cdot CO\cdot NH_2$, can be crystallised from hot water and melts at 187—188°; the *hydrochloride* crystallises from hot water, and the *benzoyl* derivative crystallises from dilute alcohol in small nodules and melts at 97°. The properties of ι-aminodecoic acid and its derivatives thus prepared are quite different from those ascribed by Krafft to the ι-aminodecoic acid prepared from his so-called decamethyleneimine (Krafft and Phookan, Abstr., 1892, 1180). It is probable, therefore, that decamethyleneimine does not exist, and that the reaction between functional groups in the same molecule is not a periodic function of the position of these groups. M. A. W.

Preparation of Pure Piperidine.

DANIEL VORLÄNDER and THEODOR WALLIS (*Annalen*, 1906, **345**, 277—288. Compare this vol., i, 729, 730).—The velocity of oxidation of the purest commercial piperidine is so great, in comparison with that of diethylamine, as to render probable the occurrence of easily oxidisable impurities in the former. A purification can be effected by twice shaking an aqueous solution of piperidine (125 grams per litre) and sulphuric acid (250 grams per litre) with 70 grams of powdered potassium permanganate, the first time for ten minutes and the second time, with the recovered piperidine, for two to three hours. A better method is to treat nitrosopiperidine in acetone with solid permanganate for one to two days in the cold, or for three to four hours at a higher temperature. The piperidine recovered from the nitroso-compound in toluene by hydrogen chloride has a constant velocity of oxidation; the acetyl derivative boils at 223°, the hydrochloride melts at 245° (corr.), and the platinichloride at 201·5° (corr.).

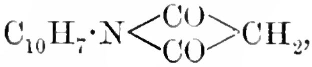
From the precipitate obtained from the acetone solution during the oxidation, a dibasic *nitroso-acid* can be isolated, having the composition

$C_3H_6ON_2(CO_2H)_2$, melting at 79°, and showing Liebermann's reaction. A neutral, colourless, crystalline *substance*, $C_5H_{10}O_2NCl$ or $C_5H_{12}O_2NCl$, was also isolated; it melts at 212° and yields ethyl acrylate when heated. The presence of a partially hydrogenated pyridine in commercial piperidine was also indicated by the behaviour of acetylpiperidine towards bromine. The crude substance reacts with bromine to the extent of 17·5 per cent., whereas the acetyl compound obtained from purified piperidine does not react at all.

The oxidation velocity of other secondary amines, purified in a similar manner, is only slightly changed, except in the case of dipropylamine, the constant for which falls to about one-quarter of its original value. C. S.

Transformation of Quinoline into 2-Methylindole. MAURICE PADOA and A. CARUGHI (*Atti R. Accad. Lincei*, 1906, [v], **15**, ii, 113—118. Compare this vol., i, 530, 695).—When a mixture of quinoline vapour and hydrogen is passed through a tube containing reduced nickel at a temperature of 260—280°, one part of the quinoline is converted into 2-methylindole and, after the opening of the closed nucleus, the remainder in part loses one carbon atom and in part two carbon atoms, giving rise to methyl-*o*-toluidine and *o*-toluidine. No methylindoline is formed in the reaction. T. H. P.

Ring-formation. II. RICHARD MEYER (*Annalen*, 1906, **347**, 17—54. Compare Abstr., 1903, i, 442).—The investigation of the action of dibasic acids on *o*-, *m*-, and *p*-diamines has been continued.

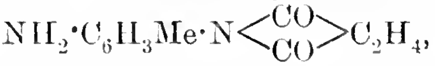
[With G. VON LUTZAU.]—Malonanilide is readily obtained from aniline and excess of ethyl malonate. α-Malon-naphthil,  $C_{10}H_7\cdot N{<}{}^{CO}_{CO}{>}CH_2$, is formed when α-naphthylamine and ethyl malonate are heated for some hours. It crystallises in needles, melts above 300°, and is soluble in alkali hydroxides (compare Whiteley, Trans., 1903, **83**, 24).

o-*Phenylenemalonamide*, prepared from *o*-phenylenediamine hydrochloride and the calculated quantity of sodium carbonate in presence of excess of ethyl malonate, crystallises in needles melting above 300°. The corresponding *derivative* of *o*-tolylenediamine crystallises in needles melting above 300°. No definite product could be obtained from *m*-phenylenediamine and ethyl malonate, but *m*-tolylenediamine [$Me:(NH_2)_2 = 1:2:4$] and ethyl malonate yield *ethyl* m-*tolylenedimalonamate*, $C_6H_3Me(NH\cdot CO\cdot CH_2\cdot CO_2Et)_2$, which is a white, amorphous powder melting at 110—113°. *p*-Phenylenediamine and ethyl malonate yield the similarly constituted *compound*,

$$C_6H_4(NH\cdot CO\cdot CH_2\cdot CO_2Et)_2,$$

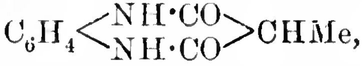
which crystallises in needles and melts at 164°.

Aniline and ethyl succinate yield succinanil, similarly α-naphthylamine yields α-succinonaphthil, but β-naphthylamine gives the *ester* of *ethyl β-naphthylsuccinamate*, $C_{10}H_7NH\cdot CO\cdot C_2H_4\cdot CO_2Et$, which crystallises in needles and melts at 99—100°. The condensation products prepared from *o*-phenylenediamine or *o*-tolylenediamine and ethyl succinate could not be purified satisfactorily. From *m*-phenylenediamine and ethyl succinate, a *compound* is obtained, crystallising in needles and melting at 205°, the chemical nature of which could not be established; with ammonia it yields m-*phenylenedisuccinamide*, $C_6H_4(NH\cdot CO\cdot C_2H_4\cdot CO\cdot NH_2)_2$, which crystallises in needles melting and decomposing at 245°. m-*Aminotolylsuccinimide*,



$$NH_2\cdot C_6H_3Me\cdot N<\genfrac{}{}{0pt}{}{CO}{CO}>C_2H_4,$$

is formed from *m*-tolylenediamine and crystallises in needles melting at 256—259°. *p*-Phenylenediamine yields *p*-aminosuccinanil (*loc. cit.*).

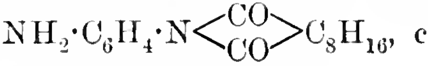
[With P. JAEGER.]—With ethyl *iso*succinate, the diamines yield similar compounds. o-*Phenylene*iso*succinimide*,  $C_6H_4<\genfrac{}{}{0pt}{}{NH\cdot CO}{NH\cdot CO}>CHMe$, crystallises in yellow plates, melting above 350°; at the same time, a *base*, $CHMe(CO\cdot NH\cdot C_6H_4\cdot NH_2)_2$, which is purified in the form of a *picrate*, is produced; the latter crystallises in yellow plates and melts and decomposes at 245—250°; the base, which could not be purified, crystallises in slender needles.

m-Phenylenediamine and ethyl *iso*succinate yield an insoluble *compound* melting at 275—280°. From *p*-phenylenediamine, *ethyl* p-*phenylenediisosuccinamate*, $C_6H_4(NH\cdot CO\cdot CHMe\cdot CO_2Et)_2$, is formed. It crystallises in needles and melts at 180—181°. The condensation product from *m*-tolylenediamine could not be isolated in the pure state. *o*-Tolylenediamine yields similarly a mixture of o-*tolylene*iso*succinamide* and the basic *di*-o-*aminotolyl*iso*succinamide*, which are separated by treatment with dilute acetic acid; the former crystallises in needles or plates, the latter in needles, and yields a *picrate* which crystallises in yellow needles melting and decomposing at 235—240°.

Ethyl adipate reacts with *o*-phenylenediamine, yielding in small amount a basic, crystalline substance which could not be purified.

[With JOH. MAIER.]—Ethyl sebacate yields with *o*-phenylenediamine two compounds: o-*phenylenesebacamide*,  $C_6H_4<\genfrac{}{}{0pt}{}{NH\cdot CO}{NH\cdot CO}>C_8H_{16}$, crystallises in needles melting at 134—135°, and is indifferent towards both acids and bases. *Di*-o-*aminophenylsebacamide*,

$$C_8H_{16}(CO\cdot NH\cdot C_6H_4\cdot NH_2)_2,$$

crystallises in needles melting above 320°. *Ethyl* m-*phenylenedisebacate*, $C_6H_4(NH\cdot CO\cdot C_8H_{16}\cdot CO_2Et)_2$, is prepared by the condensation of *m*-phenylenediamine with the ester, and crystallises in microscopic needles melting at 97°; at the same time a yellow, insoluble powder is formed. *p*-Phenylenediamine and ethyl sebacate yield several products, of which p-*aminosebacanil*,  $NH_2\cdot C_6H_4\cdot N<\genfrac{}{}{0pt}{}{CO}{CO}>C_8H_{16}$, can be isolated; it crystallises in needles melting at 150—151°.

[With P. JAEGER.]—The condensations of the chlorides of dibasic acids with aromatic diamines have been investigated. With succinyl chloride, *o*-phenylenediamine yields *di*-o-*aminophenylsuccinamide*, whilst *m*-phenylenediamine and *p*-phenylenediamine do not give condensation products, but merely succinates of the base. With *o*-tolylenediamine, *di*-o-*aminotolylsuccinamide*, $C_2H_4(CO\cdot NH\cdot C_6H_3Me\cdot NH_2)_2$, is formed, and crystallises in needles melting above 320°; the *hydrochloride* was analysed.

Adipic chloride and *o*-phenylenediamine yield *di*-o-*aminophenyl*-

adipamide, which was isolated as *hydrochloride*; the latter crystallised in long needles.

From phthalyl chloride and *o*-phenylenediamine, *di-o-aminophenylphthalamide,* $C_6H_4(CO\cdot NH\cdot C_6H_4\cdot NH_2)_2$, was prepared as colourless needles. At the same time, *o*-phenylenephthalamide was formed, and also *o*-phenylenediphthalimide, the latter being generally the main product of the reaction. Phthalyl chloride and *o*-tolylenediamine gave *o* tolylenediphthalimide. Phthalyl chloride and *p*-phenylenediamine yield *p*-aminophthalanil and p-*phenylenediphthalimide,*

$$C_6H_4\left(N\genfrac{<}{>}{0pt}{}{CO}{CO}C_6H_4\right)_2,$$

which crystallises in needles or in rhombic plates and melts at 356°.

K. J. P. O.

Constitution of Nitroimines and Action of Phenylcarbimide on Methylnitroamine. Roland Scholl (*Annalen*, 1906, **345**, 363—384. Compare Abstr., 1905, i, 181; Angelucci, *ibid.*, i, 801; Angeli and Castellana, this vol., i, 162).—In addition to the evidence adduced previously (*loc. cit.*), the following arguments are advanced in favour of the nitroimine formula, $>CH\cdot\overset{|}{C}:N\cdot NO_2$. (1) The behaviour of the nitroimines towards alkalis resembles that of secondary nitroamines. (2) The fact that the nitroimines are pseudo-acids and yield *N*- and *O*-alkyl derivatives cannot be brought into line with Angeli and Castellana's "pernitroso" formula. (3) Reducing agents generally eliminate an atom of nitrogen; in some cases, however, hydrazine derivatives are obtained. (4) Nitroimines, as a class, give the Thiele-Lachmann nitroamine reaction; the nitroimines obtained from the oximes of pinacolin, santonin, menthone, and mesityl oxide give, like most nitroamines, the Liebermann reaction. Camphornitroimine gives colour reactions with phenol and sulphuric acid, but the author does not assert positively that these are due to Liebermann's reaction. (5) The occurrence of camphanazine, nitrogen, camphene, and camphoroxime among the reduction products of camphornitroimine can be explained rationally by the nitroimine formula, and does not require the assumption of the existence of the otherwise quite unknown "pernitroso" group.

[With Karl Holdermann.]—*α-Nitro-β-phenyl-α-methylcarbamide,* $NHPh\cdot CO\cdot N(NO_2)Me$, is obtained by the reaction of methylnitroamine and "active" phenylcarbimide (phenylcarbimide containing phenylcarbamate), dry ether being added when the temperature rises to 35—40°. With ordinary phenylcarbimide the reaction proceeds slowly, but more rapidly after the addition of a small quantity of carbamide. The colourless crystals, after the removal of *s*-diphenylcarbamide by acetone and light petroleum, sinter at 68° and melt and decompose at 74·5—75°. It gives Liebermann's reaction, is decomposed by boiling water, and with ammonia (or aniline) in ether at the ordinary temperature yields phenylcarbamide (or diphenylcarbamide) and methylnitroamine.

s-*Nitrophenylmethylcarbamide,* $NO_2\cdot C_6H_4\cdot NH\cdot CO\cdot NHMe$, results from the action of ethyl nitrate on *s*-phenylmethylcarbamide in concentrated sulphuric acid at −5°. The yellow product is boiled with one per cent. sodium hydroxide, cooled, and the residue crystallised from hot acetic acid. The substance forms colourless prisms, becomes yellow at 190—200°, and melts at 230—231°. Hot dilute sodium hydroxide solution dissolves it to a yellow solution, from which the substance is recovered unchanged on cooling. The presence of the nitro-group in the benzene nucleus is deduced from the fact that the substance gives neither the Liebermann nor the Thiele-Lachmann nitroamine reaction.

s-Dinitrophenylmethylcarbamide, $C_6H_3(NO_2)_2\cdot NH\cdot CO\cdot NHMe$, results when twice the quantity of ethyl nitrate is used in the preceding preparation; it forms yellow needles, melts and decomposes at 206—207°, and resembles the preceding compound in its behaviour. C. S.

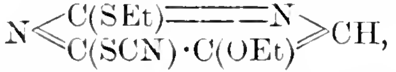
Constitution of Scholl's Nitroimines. OTTORINO ANGELUCCI (*Gazzetta*, 1906, **36**, i, 627—628. Compare Abstr., 1905, i, 801).—The author criticises the work of Scholl (preceding abstract), who states that the nitroimines react with secondary amines according to the equation $:C:N\cdot NO_2 + NH_2R = :C:NR + H_2NO_2 \longrightarrow H_2O + N_2O$. In the cold, however, camphornitroimine reacts with methylamine, giving water and nitrous oxide, which products cannot be regarded as derived from the decomposition of the nitroamide, since this is stable under the conditions of the experiment.

Further, Scholl states that all nitroimines give the reaction of Liebermann and that of Thiele and Lachmann. The author finds that pernitrosocamphor gives no trace of Liebermann's reaction.

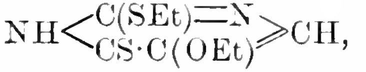
T. H. P.

Benzenesulphomethylguanidine. D. ACKERMANN (*Zeit. physiol. Chem.*, 1906, **48**, 382. Compare this vol., ii, 505).—Methylguanidine reacts with benzenesulphonic chloride yielding *benzenesulphomethylguanidine*, which melts at 184°; its solubility in water at the ordinary temperature is 0·04 in 100. J. J. S.

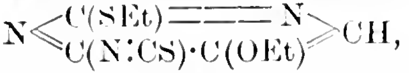
Pyrimidines: Action of Potassium Thiocyanate on Imide Chlorides. XV. TREAT B. JOHNSON and ELMER V. McCOLLUM (*Amer. Chem. J.*, 1906, **36**, 136—148. Compare this vol., i, 704; Wheeler and Merriam, Abstr., 1901, i, 514; Wheeler and Bristol, Abstr., 1905, i, 483).—*6-Thiocyano-5-ethoxy-2-ethylthiolpyrimidine*,



$$N{<}\begin{matrix}C(SEt)\!=\!\!=\!\!=\!N\\C(SCN)\cdot C(OEt)\end{matrix}{>}CH,$$

prepared by boiling 6-chloro-5-ethoxy-2-ethylthiolpyrimidine with potassium thiocyanate in 95 per cent. alcoholic solution, crystallises from alcohol in lemon-yellow prisms, melts at 66—67°, and dissolves in concentrated hydrochloric acid, being reprecipitated by alkali hydroxides or on dilution. It reacts with thiobenzoic or thioacetic acid with development of heat, forming *6-thio-5-ethoxy-2-ethylthiolpyrimidine*,  $NH{<}\begin{matrix}C(SEt)\!=\!N\\CS\cdot C(OEt)\end{matrix}{>}CH$, which is prepared also by boiling 6-chloro-5-ethoxy-2-ethylthiolpyrimidine with alcoholic potassium sulphide; it crystallises from alcohol in yellow prisms and melts at 144—145°.

6-*Thiocarbimido-5-ethoxy-2-ethylthiolpyrimidine*,



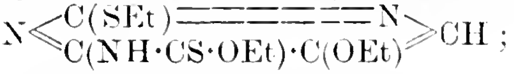
$$\mathrm{N}{<}\begin{matrix}\mathrm{C(SEt)}=\!=\!=\!=\mathrm{N}\\ \mathrm{C(N{:}CS)\cdot C(OEt)}\end{matrix}{>}\mathrm{CH},$$

is formed when the 6-thiocyanopyrimidine is heated at 105—110°; it solidifies over concentrated sulphuric acid, melts at 45—50°, boils at 228—235° under 20—23 mm. pressure, is exceedingly hygroscopic, and when treated with ammonia yields 6-*thiocarbamido-5 ethoxy-2-ethylthiolpyrimidine*,

$$\mathrm{N}{<}\begin{matrix}\mathrm{C(SEt)}=\!=\!=\!=\!=\!=\!=\mathrm{N}\\ \mathrm{C(NH\cdot CS\cdot NH_2)\cdot C(OEt)}\end{matrix}{>}\mathrm{CH},$$

which crystallises from alcohol in yellow prisms and melts at 172°.

When 6-chloro-5-ethoxy-2-ethylthiolpyrimidine is boiled with potassium thiocyanate in alcoholic solution, the cyanothiol formed changes slowly into the thiocarbimido-derivative, which reacts with alcohol, forming *ethyl 5-ethoxy 2-ethylthiolpyrimidine-6-thiocarbamate*,



$$\mathrm{N}{<}\begin{matrix}\mathrm{C(SEt)}=\!=\!=\!=\!=\!=\mathrm{N}\\ \mathrm{C(NH\cdot CS\cdot OEt)\cdot C(OEt)}\end{matrix}{>}\mathrm{CH};$$

this crystallises in long prisms, melts at 93—94°, volatilises to some extent when evaporated with alcohol, and is soluble in aqueous sodium hydroxide.

n-*Propyl 5-ethoxy-2-ethylthiolpyrimidine-6-thiocarbamate*,

$$\mathrm{OEt\cdot C_4N_2H(SEt)\cdot NH\cdot CS\cdot OPr^a},$$

formed similarly by boiling 6-chloro-5-ethoxy-2-ethylthiolpyrimidine with potassium thiocyanate in *n*-propyl-alcoholic solution, crystallises in small prisms and melts at 56—57°.

The following thiocarbamido-derivatives are prepared by heating 6-thiocyano-5-ethoxy-2-ethylthiolpyrimidine at 150—160° and treating the product with the aromatic base in benzene solution. 6-*Phenylthiocarbamido-5-ethoxy-2-ethylthiolpyrimidine*,

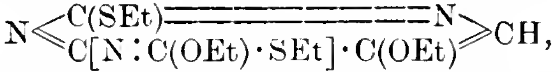
$$\mathrm{OEt\cdot C_4N_2H(SEt)\cdot NH\cdot CS\cdot NHPh},$$

forms distorted prisms and melts at 82—83°. 6-p-*Tolylthiocarbamido-5-ethoxy-2-ethylthiolpyrimidine*, $C_{16}H_{20}ON_4S_2$, forms stellate clusters of needles and melts at 115°. 6-o-*Tolylthiocarbamido-5-ethoxy-2-ethylthiolpyrimidine*, $C_{16}H_{20}ON_4S_2$, crystallises in rhombic prisms and melts at 129—130°. 6-p-*Anisylthiocarbamido-5-ethoxy-2-ethylthiolpyrimidine*, $OEt\cdot C_4N_2H(SEt)\cdot NH\cdot CS\cdot NH\cdot C_6H_4\cdot OMe$, crystallises from alcohol in rhombic prisms and melts at 122—123°. 6-m-*Nitrophenylthiocarbamido-5-ethoxy-2-ethylthiolpyrimidine*, $C_{15}H_{17}O_3N_5S_2$, forms slender prisms and melts at 161°. G. Y.

Pyrimidines: Formation of Purines from Carbamidopyrimidines. XVI. TREAT B. JOHNSON and ELMER V. McCOLLUM (*Amer. Chem. J.*, 1906, **36**, 149—159. Compare preceding abstract and this vol., i, 704).—*Ethyl formylglycollate*, $OEt\cdot CH(COH)\cdot CO_2Et$, is obtained on addition of hydrochloric acid to its sodium salt as a colourless oil which boils at 115—118° under 35 mm. pressure.

2 : 6-Dioxy-5-ethoxypyrimidine is readily prepared by boiling 5-ethoxy-2-methylthiolpyrimidine with hydrochloric acid.

Ethyl 5-ethoxy-2-ethylthiolpyrimidine-6-iminothiocarbonate,



$$\mathrm{N}{<}\begin{matrix}\mathrm{C(SEt)}=\!=\!=\!=\!=\!=\!=\mathrm{N}\\ \mathrm{C[N{:}C(OEt)\cdot SEt]\cdot C(OEt)}\end{matrix}{>}\mathrm{CH},$$

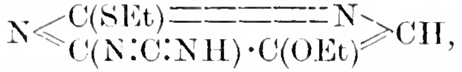
is prepared by the action of ethyl bromide and sodium on ethyl

5-ethoxy-2-ethylthiolpyrimidine-6-thiocarbamate in alcoholic solution it is obtained as an oil which reacts with ammonia in alcoholic solution, forming 6-*ψ-ethylcarbamido-5-ethoxy-2-ethylthiolpyrimidine*,

$$\mathrm{OEt\cdot C_4N_2H(SEt)\cdot N{:}C(NH_2)\cdot OEt};$$

this crystallises from light petroleum, melts at 77°, and is converted slowly by concentrated hydrochloric acid into 6-*carbamido-5-ethoxy-2-ethylthiolpyrimidine*, $\mathrm{OEt\cdot C_4N_2H(SEt)\cdot NH\cdot CO\cdot NH_2}$, which forms prismatic crystals and melts and decomposes at 166—167°.

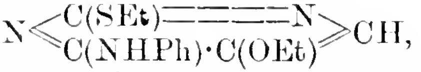
6-*Cyanamino-5-ethoxy-2-ethylthiolpyrimidine*,



$$\mathrm{N}\Big\langle\begin{array}{l}\mathrm{C(SEt)=\!=\!=\!=\!=\!=N}\\ \mathrm{C(N{:}C{:}NH)\cdot C(OEt)}\end{array}\Big\rangle\mathrm{CH},$$

prepared by boiling 6-ψ-ethylcarbamido-5-ethoxy-2-ethylthiolpyrimidine with sodium in benzene solution for forty hours, crystallises in white prisms, melts and effervesces slightly at 167—168°, is soluble in aqueous alkali hydroxides, is reprecipitated by acids, and is decomposed slowly by boiling water. The *hydrochloride* forms slender prisms and melts and decomposes at 175—180°.

6-*Anilino-5-ethoxy-2-ethylthiolpyrimidine*,

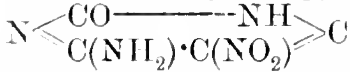


$$\mathrm{N}\Big\langle\begin{array}{l}\mathrm{C(SEt)=\!=\!=\!=\!=N}\\ \mathrm{C(NHPh)\cdot C(OEt)}\end{array}\Big\rangle\mathrm{CH},$$

formed by boiling 6-chloro-5-ethoxy-2-ethylthiolpyrimidine with aniline in alcoholic solution, crystallises from light petroleum in large prisms and melts at 60°. 6-p-*Toluidino-5-ethoxy-2-ethylthiolpyrimidine* crystallises in long prisms, melts at 72°, and yields a *hydrochloride*, $\mathrm{C_{15}H_{19}ON_3S,HCl}$, which forms hair-like crystals and melts and decomposes at 105—106°. 6-o-*Toluidino-5-ethoxy-2-ethylthiolpyrimidine*, $\mathrm{C_{15}H_{19}ON_3S}$, crystallises from alcohol in flat prisms and melts at 80°; the *hydrochloride*, $\mathrm{C_{15}H_{19}ON_3S,HCl}$, forms prisms and decomposes at 140—145°, or when dissolved in water. 6-p-*Anisidino 5-ethoxy-2-ethylthiolpyrimidine*,

$$\mathrm{OEt\cdot C_4N_2H(SEt)\cdot NH\cdot C_6H_4\cdot OMe},$$

crystallises from alcohol in stout prisms and melts at 68—69°; the *hydrochloride*, $\mathrm{C_{15}H_{19}O_2N_3S,HCl}$, forms prismatic crystals. 6-m-*Nitroanilino-5-ethoxy-2-ethylthiolpyrimidine*, $\mathrm{C_{14}H_{16}O_3N_4S}$, crystallises in long needles and melts at 125°; the *hydrochloride* melts and decomposes at 125—135°. G. Y.

Pyrimidines: 5 Nitrocytosine and its Reduction to 5:6-Diamino-2-oxypyrimidine. XVII. Treat B. Johnson, Carl O. Johns, and Frederick W. Heyl (*Amer. Chem. J.*, 1906, **36**, 160—177).—Nitrocytosine (Wheeler and Johnson, Abstr., 1904, i, 624), which is formed in an 83·5 per cent. yield by the action of nitric acid of sp. gr. 1·5 on 6-amino-2-ethylthiolpyrimidine, is 5-nitro-6-amino-2-oxypyrimidine,  $\mathrm{N}\Big\langle\begin{array}{l}\mathrm{CO-\!\!-\!\!-\!\!-NH}\\ \mathrm{C(NH_2)\cdot C(NO_2)}\end{array}\Big\rangle\mathrm{CH}$, as (1) it yields nitrouracil when heated with 20 per cent. sulphuric acid in a sealed tube at 185—197°, or when heated with nitrosyl chloride in aqueous hydrochloric acid solution in a sealed tube at 85—95°, and (2) it does not react with bromine. The *hydrochloride* of 5-nitrocytosine,

$$\mathrm{C_4H_4O_3N_4,HCl},$$

forms clusters of prisms and does not decompose below 300°.

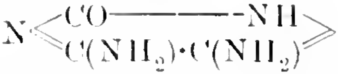
The action of nitric acid of sp. gr. 1·5 on 5-bromo-6-amino-2-ethylthiolpyrimidine leads to the formation of 5-bromocytosine.

5-Nitro-6-phenylcarbamido-2-oxypyrimidine,

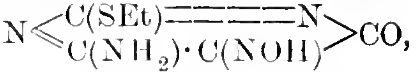
$$\mathrm{N}{<}\begin{matrix}\mathrm{CO}\text{————————}\mathrm{NH}\\ \mathrm{C(NH\cdot CO\cdot NHPh)\cdot C(NO_2)}\end{matrix}{>}\mathrm{CH},$$

formed by heating 5-nitrocytosine with phenylthiocarbimide at 100°, decomposes, but does not melt, above 215°, and is insoluble in all solvents.

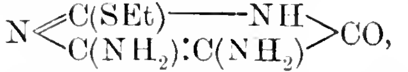
When boiled with acetic anhydride, 5-nitrocytosine yields mixtures of the *mono-* and *di-acetyl* derivatives; the latter, $C_8H_8O_5N_4$, forms needle-like prisms and decomposes at 273—275°.

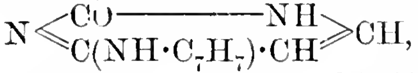
5 : 6-*Diamino-2-oxypyrimidine*,  $\mathrm{N}{<}\begin{matrix}\mathrm{CO}\text{————}\mathrm{NH}\\ \mathrm{C(NH_2)\cdot C(NH_2)}\end{matrix}{>}\mathrm{CH},H_2O$, is prepared by reduction of 5-nitrocytosine with aluminium amalgam and water below 35°; it forms clusters of prisms, loses H_2O at 120—130°, decomposes above 230°, forms an insoluble, red precipitate with potassium bismuth iodide, reduces platinum, gold, silver, and Fehling's solutions, has an alkaline reaction to litmus, and is precipitated by phosphotungstic acid. The *picrate*, $C_4H_6ON_4,C_6H_3O_7N_3$, forms spherical aggregates of prisms, commences to become brown at about 170°, and decomposes when more highly heated; the *mercurichloride*, $C_4H_6ON_4,HgCl_2$, was analysed.

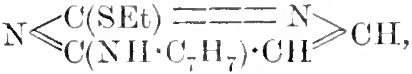
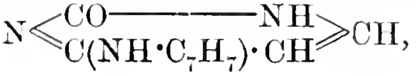
6-*Amino-5-nitroso-2-methylthiol-4-oxypyrimidine*,



$$\mathrm{N}{<}\begin{matrix}\mathrm{C(SEt)}\text{====}\mathrm{N}\\ \mathrm{C(NH_2)\cdot C(NOH)}\end{matrix}{>}\mathrm{CO},$$

prepared by the action of sodium nitrite and glacial acetic acid on 6-amino-2-methylthiol-4-oxypyrimidine in aqueous sodium hydroxide solution, is reduced by ammonium sulphide to 5 : 6-*diamino-2-methylthiol-4-oxypyrimidine*,  $\mathrm{N}{<}\begin{matrix}\mathrm{C(SEt)}\text{———}\mathrm{NH}\\ \mathrm{C(NH_2){:}C(NH_2)}\end{matrix}{>}\mathrm{CO}$, which crystallises in needles or prisms, melts and decomposes at 215—216°, is readily soluble in alcohol, and becomes red when exposed to air.

6-p-*Toluidino-2-ethylthiolpyrimidine*,  $\mathrm{N}{<}\begin{matrix}\mathrm{C(SEt)}\text{===}\mathrm{N}\\ \mathrm{C(NH\cdot C_7H_7)\cdot CH}\end{matrix}{>}\mathrm{CH}$, prepared by heating 6-chloro-2-ethylthiolpyrimidine with *p*-toluidine in benzene solution, crystallises in prisms, melts at 104°, and is readily soluble in alcohol or benzene; the *hydrochloride*, $C_{13}H_{15}N_3S,HCl$, crystallises in needles and decomposes at 198—207°. When boiled with hydrochloric acid, the base yields 6-p-*toluidino-2-oxypyrimidine*,  $\mathrm{N}{<}\begin{matrix}\mathrm{CO}\text{————}\mathrm{NH}\\ \mathrm{C(NH\cdot C_7H_7)\cdot CH}\end{matrix}{>}\mathrm{CH}$, which melts and decomposes at 288—289°; the *hydrochloride*, $C_{11}H_{11}ON_3,HCl$, forms microscopic prisms and decomposes at 180—190°.

6-o-*Toluidino-2-ethylthiolpyrimidine*,  $\mathrm{N}{<}\begin{matrix}\mathrm{C(SEt)}\text{===}\mathrm{N}\\ \mathrm{C(NH\cdot C_7H_7)\cdot CH}\end{matrix}{>}\mathrm{CH}$, prepared from 6-chloro-2-ethylthiolpyrimidine and *o*-toluidine, crystallises from alcohol in prisms and melts at 87°; the *hydrochloride* $C_{13}H_{15}N_3S,HCl$, forms granular crystals and melts and decomposes at 230—232°. When boiled with hydrochloric acid, the base forms 6-o-*toluidino-2-oxypyrimidine*,  $\mathrm{N}{<}\begin{matrix}\mathrm{CO}\text{————}\mathrm{NH}\\ \mathrm{C(NH\cdot C_7H_7)\cdot CH}\end{matrix}{>}\mathrm{CH}$, which crystallises in stellate clusters of prisms and decomposes at 262° ; the *hydrochloride*, $C_{11}H_{11}ON_3,HCl$, forms lenticular crystals and decomposes at 227—231°.

6-p-*Anisidino-2-ethylthiolpyrimidine*, $SEt{\cdot}C_4N_2H_2{\cdot}NH{\cdot}C_6H_4{\cdot}OMe$, is obtained as an oil ; the *hydrochloride*, $C_{13}H_{15}ON_3S,HCl$, crystallises in needles and melts and decomposes at 200—201°. 6-p-*Anisidino-2-oxypyrimidine*, $C_{11}H_{11}O_2N_3$, melts at 262° ; the *hydrochloride*,

$$C_{11}H_{11}O_2N_3,HCl,$$

decomposes at 145—165°.

6-m-*Nitro-2-ethylthiolpyrimidine*, $SEt{\cdot}C_4N_2H_2{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2$, melts at 175° ; the *hydrochloride*, $C_{12}H_{12}O_2N_4S,HCl$, forms needles and decomposes at 140—155°. 6-m-*Nitro-2-oxypyrimidine*, $C_{10}H_8O_3N_4$, is formed by boiling the preceding compound with hydrobromic acid ; it crystallises in needle-like prisms and decomposes above 275°.

G. Y.

Metbylene-green. Eugène Grandmougin and E. Walder (*Zeit. Farb. Ind.*, 1906, **5**, 285—286).—The view that methylene-green is nitromethylene-blue (Gnehm and Walder, this vol., i, 390) is confirmed by the fact that it can be prepared by nitrating methylene-blue dissolved in 40 per cent. acetic acid with 50 per cent. nitric acid. The dye is separated in the form of the *zincochloride*,

$$2C_{16}H_{17}O_2N_4SCl,ZnCl_2,$$

which forms a dark brownish-violet, non-crystalline powder. The *hydriodide*, $C_{16}H_{16}O_2N_4S,HI,H_2O$, forms long, violet needles and crystallises well from water.

W. A. D.

Aromatic Azocyanamides. Paul Pierron (*Compt. rend.*, 1906, **143**, 340—344).—*Benzeneazo*-p-*cyananilide*, $Ph{\cdot}N_2{\cdot}C_6H_4{\cdot}NH{\cdot}CN$, prepared by the action of diazobenzene chloride on the sodium derivative of cyananilide according to the equation $Ph{\cdot}N_2Cl + NHPh{\cdot}CN = Ph{\cdot}N_2{\cdot}C_6H_4{\cdot}NH{\cdot}CN + NaCl$, or by the action of an alcoholic solution of cyanogen chloride or bromide on *p*-aminoazobenzene in the presence of alkali hydrogen carbonates, forms yellow, flattened needles melts at 163°, is readily soluble in alcohol, slightly so in benzene or ether, and almost insoluble in water ; its alkaline solutions dye wool, silk, or mordanted cotton light yellow ; it is hydrolysed by dilute acids, yielding the corresponding carbamide, *benzeneazo*-p-*phenylcarbamide*, $Ph{\cdot}N_2{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}NH_2$, which crystallises from alcohol in brownish-yellow needles, melts at 231°, is insoluble in water, slightly soluble in ether, chloroform or benzene, more so in alcohol. The *benzoyl* derivative, $Ph{\cdot}N_2{\cdot}C_6H_4{\cdot}NBz{\cdot}CN$, forms short, hard, orange prisms, melts at 161°, is soluble in alcohol, and slightly so in benzene. Benzeneazo-*p*-cyananilide is reduced by stannous chloride, yielding aniline and *p*-aminophenylcarbamide, and reacts with hydroxylamine to form *p*-aminoazobenzene and phenylcarbamide.

Benzeneazo-p-*cyano*-o-*toluidide*, $Ph{\cdot}N_2{\cdot}C_6H_3Me{\cdot}NH{\cdot}CN$, prepared similarly to the above compound, which it closely resembles, melts at 159° ; the *carbamide* and *benzoyl* derivatives melt at 207° and 141° respectively.

Benzeneazo-p-cyano m *toluidide*, $Ph{\cdot}N_2{\cdot}C_6H_3Me{\cdot}NH{\cdot}CN$, forms light yellow, pliable, silky needles, and melts at 118—119° when gently or at 105° when rapidly heated; the *carbamide* and *benzoyl* derivatives melt at 152° and 134° respectively, and form long, flexible needles, the former dull reddish-yellow, the latter brilliant orange. *Benzeneazo α-cyanonaphthylamide*, $Ph{\cdot}N_2{\cdot}C_{10}H_6{\cdot}NH{\cdot}CN$, forms a violet-red powder with a green reflex, melts indefinitely at 176—180°, and is very hygroscopic; the *carbamide* derivative melts at 253°.

Benzeneazo-o-ethoxy-p-cyanoanilide, $Ph{\cdot}N_2{\cdot}C_6H_3(OEt){\cdot}NH{\cdot}CN$, melts at 121° and crystallises from a mixture of light petroleum and benzene in orange-yellow needles; the *carbamide* derivative forms light yellow needles and melts at 206°.

p-Cyanotoluidide forms an unstable compound, probably the diazo-cyanamide, $Ph{\cdot}N_2{\cdot}N(CN){\cdot}C_6H_4Me$, with diazobenzene chloride, which rapidly decomposes, yielding a tarry, black mass containing the original cyanamide, the corresponding carbamide, and *p*-hydroxyazobenzene. The following equations indicate the probable course of the reactions:

$$Ph{\cdot}N_2{\cdot}N(CN){\cdot}C_6H_4Me + H_2O = PhOH + N_2 + C_6H_4Me{\cdot}NH{\cdot}CN;$$
$$Ph{\cdot}N_2{\cdot}N(CN){\cdot}C_6H_4Me + PhOH = Ph{\cdot}N_2{\cdot}C_6H_4{\cdot}OH + C_6H_4Me{\cdot}NH{\cdot}CN.$$

M. A. W.

Salts of Benzeneazophenyltrimethylammonium. DANIEL VORLÄNDER, A. LOGOTHETIS, and A. J. PEROLD (*Annalen*, 1906, **345**, 303—314).—The iodide, prepared from methyl iodide and dimethylaminoazobenzene, separates from water at 80° in orange-yellow crystals which melt at 184°, and from methyl or amyl alcohol in brown or orange-red crystals which melt at 173°.

The iodide, precipitated by potassium iodide from a solution of benzeneazophenyltrimethylammonium chloride, melts at 178°, and after crystallisation from alcohol at 175°. By crystallisation from water, the melting point of the former substance rises to 183°, whereas that of the latter, after repeated crystallisation from alcohol, falls to 170—173°.

The *bromide*, prepared by shaking the iodide and silver bromide in water or alcohol, separates from water at 80° in crystals which melt at 196°, and from alcohol in leaflets melting at 192°. The leaflets occur in three forms. All these crystals, according to crystallographic measurements, belong to the same, probably to the rhombic, system.

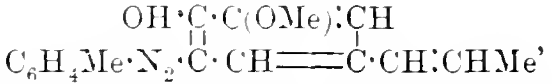
The chloride, obtained from the iodide and silver chloride, separates from water in orange prisms, melts at 194°, and contains 1—2 mols. H_2O. The *zinc* salt, $(C_{15}H_{18}N_3Cl)_2,ZnCl_2$, separates from water in orange-yellow plates, melts at 201°, and contains $2H_2O$. The *platinichloride*, $(C_{15}H_{18}N_3)_2PtCl_6$, forms orange-yellow needles and melts and decomposes at 195—198°. The *nitrate* melts at 216°. The *picrate* forms yellow needles. The *carbonate* is obtained by evaporating in a vacuum a solution of the hydroxide saturated with carbon dioxide; it forms orange-red plates. The aqueous solution of the free base has a deep orange colour and an alkaline reaction; when freshly prepared it is odourless, but after some time acquires the odour of trimethylamine. By boiling or by evaporation in a vacuum at 30—35° the solution decomposes and yields methylated amines, ammonia, dimethylaniline, *p*-dimethylaminoazobenzene, and a substance which melts at 126—127° and is sparingly soluble in hot water.

Aniline and not methylaniline results by the reduction of benzeneazophenyltrimethylammonium chloride by stannous chloride and hydrochloric acid; the chloride is therefore an ammonium-azo-compound, $NPh{:}N{\cdot}C_6H_4{\cdot}NMe_3X$, and not a quinone phenylhydrazone. $NPhMe{\cdot}N{:}C_6H_4{:}NMe_2X$. C. S.

Isomerism among the Hydroxyazo-compounds: 5-Azo*iso*eugenols. ERNESTO PUXEDDU (*Atti R. Accad. Lincei*, 1906, [v], **15**, ii, 128—136).—The azo-derivatives of *iso*eugenol, like those of eugenol (Oddo and Puxeddu, Abstr., 1905, i, 492), have the azo-group in the 5-position, taking the position of the propenyl group as 1. The change in the nature of the C_3H_5 substituent from allyl in the eugenol compounds to propenyl in the *iso*eugenol derivatives is accompanied by considerable changes in the physical and chemical characters. Thus, the azo*iso*eugenols cannot be obtained in a crystalline condition from alcohol or other solvents. They dissolve in dilute alkali hydroxide solutions, but do not separate out, as do the azoeugenols, without the addition of carbon dioxide or a mineral acid. When heated, they decompose without showing any definite melting point. They are not reduced by phenylhydrazine. On boiling with acetic anhydride and fused sodium acetate, they yield amorphous acetyl derivatives, which, when separated by the addition of water, emit an agreeable aromatic odour resembling that of raspberries.

Benzeneazo*iso*eugenol (compare Borsche and Streitberger, Abstr., 1904, i, 1064) is obtained as a brick-red, amorphous powder, which dissolves in concentrated sulphuric acid, giving an intense brown coloration, and ignites on contact with fuming nitric acid. Its ethereal solution, on adding ethereal ferric chloride solution, assumes a brown colour.

*o-Tolueneazo*iso*eugenol*,



$$\begin{array}{l} \phantom{C_6H_4Me\cdot N_2\cdot{}}OH\cdot C\cdot C(OMe){:}CH \\ C_6H_4Me\cdot N_2\cdot C\cdot CH{=\!=}C\cdot CH{:}CHMe \end{array}$$

is a reddish-brown powder, readily soluble in the ordinary organic solvents, excepting light petroleum and carbon tetrachloride, in which it dissolves only sparingly. It begins to darken and decompose at 62°.

*m-Tolueneazo*iso*eugenol*, $C_{17}H_{18}O_2N_2$, forms a red powder which begins to decompose at about 100°, and dissolves slightly in light petroleum or carbon tetrachloride and readily in other organic solvents. Concentrated sulphuric acid dissolves it, giving an intensely brown solution, and nitric acid causes it to ignite.

*β-Naphthaleneazo*iso*eugenol*, $C_{20}H_{18}O_2N_2$, is obtained as a brick-red powder, which dissolves readily in the more common organic solvents. *α-Naphthaleneazo*iso*eugenol* is an amorphous, reddish-brown powder, which decomposes without melting.

*o-Nitrobenzeneazo*iso*eugenol* is a reddish-brown powder which begins to decompose at about 120°, and dissolves readily in organic solvents. *p-Nitrobenzeneazo*iso*eugenol* was also prepared. T. H. P.

Chemical Action of Light. ROBERTO CIUSA (*Atti R. Accad. Lincei*, 1906, [v], **15**, ii, 136—138).—On subjecting *s*-tribromodiazobenzene *syn*.-cyanide, in benzene solution, to the action of light for three days, it is completely transformed into the corresponding *anti*-compound (compare Hantzsch and Schultze, Abstr., 1895, i, 348).

T. H. P.

Action of Dilute Hydrochloric Acid on Albumins. ED. SWIRLOWSKY (*Zeit. physiol. Chem.*, 1906, **48**, 252—299. Compare Lawroff, Abstr., 1905, ii, 178).—The prolonged action of 0·5 per cent. hydrochloric acid on the following proteids at 36—38° has been investigated, care being taken that putrefaction did not occur and that proteolytic enzymes were absent: gelatin, albumin from the blood serum of horses, casein, crystallised hæmoglobin from horse's blood, and albumoses obtained from Witt's peptone. The effects produced by the acid are similar to those observed during peptic digestion, but the reaction proceeds far more slowly. Monoamino-acids or combinations of such acids are formed; these are not precipitated by phosphotungstic acid and are decomposed by 20 per cent. hydrochloric or sulphuric acid into free amino-acids. The intensity of the action is different with the different proteids. Gelatin is least readily hydrolysed, so that at the end of 150 days the presence of free amino-acids cannot be demonstrated, as is the case with the other proteids. Previous drying of the proteids does not appear to affect the hydrolysis.

J. J. S.

The Nucleic Acid from the Spermatozoa of Muræncesox cinereus. KATSUJI INOUYE (*Zeit. physiol. Chem.*, 1906, **48**, 181—184. Compare this vol., i, 55).—A nucleic acid has been isolated from the mature spermatozoa of *Muræncesox cinereus Forsk.* It appears to contain slightly more nitrogen and phosphorus than the nucleic acid from the intestine. When hydrolysed with 20 per cent. sulphuric acid, it yields lævulic acid, guanine, adenine, xanthine, hypoxanthine, cytosine, and thymine.

J. J. S.

Preparation and Composition of Myco-nucleic Acids from Yeast. WILLIAM F. BOOS (*Chem. Centr.*, 1906, i, 1833; from *Arch. exp. Path. Pharm.*, **55**, 16—20).—Nucleic acids prepared from yeast by the method adopted by Herlant (Abstr., 1900, i, 466) exhibited variations in the amount of oxygen similar to those observed by Herlant. Four different preparations gave the compositions: (1) $C_{36}H_{52}O_{14}N_{14}(P_2O_5)_2 + 8O$, (2) $C_{36}H_{52}O_{14}N_{14}(P_2O_5)_2 + 3O$, (3) and (4) $C_{36}H_{52}O_{14}N_{14}(P_2O_5)_2 + 2H_2O$. With another method of preparation in which any possible variation in the action of the potassium was avoided, a nucleic acid of the composition $C_{36}H_{52}O_{14}N_{14}(P_2O_5)_2$ was obtained.

T. H. P.

Latschinoff's Cholocamphoric Acid. THEODOR PANZER (*Zeit. physiol. Chem.*, 1906, **48**, 192—204. Compare Latschinoff, this Journal, 1880, 56, 722).—Cholocamphoric acid, obtained by the oxidation of cholic acid with nitric acid, crystallises from water in long, slender, silky needles and dissolves readily in glacial acetic acid or in 80 per cent. alcohol. When quickly heated, it turns brown at 270° and decomposes at 286°. The analytical results agree best with the formula $C_{14}H_{22}O_6$, and not the formula $C_{10}H_{16}O_4$, suggested by Latschinoff. It appears to be a tribasic acid, but a crystalline anhydride has not been prepared. When the acid is distilled with lime, a benzene hydrocarbon, $C_{11}H_{16}$, distilling at 227° (uncorr.) is obtained. When the hydrocarbon is oxidised, benzoic and phthalic acids do not appear to be formed, and it is thus probable that in both the hydrocarbon and in the acid at least three side-chains are present. The hydrocarbon is a benzene derivative, and the acid a hexamethylene compound. J. J. S.

Diamino-acids derived from Egg-albumin. LOUIS HUGOUNENQ and J. GALIMARD (*Compt. rend.*, 1906, **143**, 242—243).—By hydrolysing egg-albumin with dilute sulphuric acid in presence of sodium chloride, the authors have obtained (1) 2·14 per cent. of arginine; (2) 2·15 per cent. of lysine; (3) a white *compound*, $C_{11}H_{18}O_4N_5$, which crystallises in small needles, soluble in water, but insoluble in alcohol, and is precipitated by acid mercuric sulphate solution; it appears to be a compound of arginine with an acid amide, such as pyrrolidine-2-carboxylic acid; (4) a *compound* which is not precipitated by mercuric sulphate and yields a *hydrochloride*, $C_{10}H_{19}O_6N_5,2HCl$, crystallising in moderately hard, white prisms; this compound is probably a derivative of arginine and aspartic acid. Histidine is absent. T. H. P.

The True Nature of Lepierre's α-Glucoproteins. J. GALIMARD, L. LACOMME, and ALBERT MOREL (*Compt. rend.*, 1906, **143**, 298—300).—The constitution ascribed by Lepierre (Abstr., 1901, i, 622) to the nitrogenous compounds (glucoproteins) which he employed for the cultivation of micro-organisms is inexact; his so-called "α-glucoproteins" are mixtures of monoamino-acids (alanine, leucine, and phenylalanine) containing traces of tyrosine and non-crystalline substances (Hugounenq and Morel, this vol., i, 719), and it is these which play the most important part in the nutrition of the micro-organisms, for the nutritive value of the "glucoproteins" is destroyed when all traces of tyrosine and non-crystalline substances are removed by means of repeated crystallisations. M. A. W.

Amount of Phosphorus in Egg-albumin. KARL KAAS (*Monatsh.*, 1906, **27**, 403—409. Compare Hofmeister, Abstr., 1898, i, 390; Hopkins and Pinkus, *ibid.*, 456).—The albumin of a fresh hen's egg contained 0·155 per cent., whilst that of an egg one month old contained 0·228 per cent., of phosphorus, the difference being probably in consequence of diffusion of phosphorus from the yolk. Crystalline egg-albumin prepared by Hofmeister and Hopkins's method and Pinkus's method contained 0·919 per cent., but after elimination of the amino-groups by treatment with sodium nitrite and glacial acetic acid, 2·42 per cent., of phosphorus. Of two specimens of pure egg-albumin, the one prepared by Hofmann and Pinkus' method, and freed from ammonium sulphate by dialysis, contained 0·352 per cent. of phosphorus, whilst the other, prepared by Hammarsten's process, was free from phosphorus. G. Y.

Animal Gelatins. V. Preparation of Gelatins. WL. S. SADIKOFF (*Zeit. physiol. Chem.*, 1906, **48**, 130—139. Compare Abstr., 1904, i, 125, 126, 462; this vol., i, 224).—The various methods for the preparation and purification of gelatin are discussed. Most of these methods are tedious, remove but part of the impurities, and produce a partial decomposition of the gelatin. The following method is recommended. Pounded bones are extracted with fresh amounts of hydrochloric acid (1 : 3) for seven to eight days, and then, after washing with water, transferred to a 1—3 per cent. solution of sodium hydroxide. By this method all albumins, mucin, nucleo-proteids, &c., are dissolved, any calcium phosphate is precipitated, and fatty compounds are hydrolysed. After the alkaline liquid has been changed three times, the residue is washed with water and the hyaline mass added to a boiling 1 per cent. solution of chloroacetic acid. The gelatin-yielding substances are readily transformed into gelatin, and after filtration the gelatin may be precipitated by the aid of magnesium sulphate and then washed with water and alcohol.

Gelatin prepared by the ordinary method may be purified by washing with water and then with a cold 20 per cent. aqueous solution of magnesium sulphate. It is then dissolved in warm 20 per cent. magnesium sulphate solution, filtered hot, and to the cold filtrate is added a 0·5 per cent. solution of hydrochloric or sulphuric acid in 20 per cent. magnesium sulphate. The precipitate is removed, washed, dissolved in hot water, and very dilute acid and much alcohol are added, and then the gelatin precipitated by neutralisation with ammonia. J. J. S.

Absorption of Gallic Acid by Organic Colloids. WILLIAM P. DREAPER and ALEXANDER WILSON (*J. Soc. Chem. Ind.*, 1906, **25**, 515—518).—A detailed account of the experimental results, of which a summary has been published previously (Proc., 1906, **22**, 70). P. H.

Kyrines. MAX SIEGFRIED (*Zeit. physiol. Chem.*, 1906, **48**, 54—68. Compare Abstr., 1903, i, 586; 1905, i, 104).—Kyrines, the intermediate decomposition products of proteids by acids, are characterised by the constancy of the composition of their sulphates, by the relationship of the nitrogen precipitated by phosphotungstic acid to the total nitrogen, and by their forming characteristic phosphotungstates. Skraup and Zwerger's doubts (this vol., i, 123) as to the homogeneity of caseinokyrine are investigated, and, by following the change in rotation, the hydrolysis of casein at 100° and at 38° is compared. It is possible when mixtures of kyrine sulphate and lysine are precipitated with phosphotungstic acid to distinguish microscopically the mixed phosphotungstates. The picrates also afford a means of distinguishing caseinokyrine from lysine and arginine, the former separating always as an oil, whereas lysine picrate crystallises immediately the excess of picric acid is removed by ether.

Kyrine obtained from fibrin yields lysine, arginine, and glutamic acid on hydrolysis. Constancy in the composition of the sulphate was obtained after the ninth precipitation; 72·7 per cent. of the nitrogen was then in a form precipitable by phosphotungstic acid and about half the total was in the form of arginine. E. F. A.

Hydrolysis of Meat Extract. Karl Micko (*Zeit. Nahr. Genussm.*, 1906, **11**, 705—729).—The constituents of the mixture obtained on hydrolysing meat extract were separated by Emil Fischer's ester method, alanine, leucine, glycine, and valeric acid being obtained in the earlier fractions. Considerable quantities of lactic acid and of succinic acid were also proved to be present. In all about 20 per cent. of the organic matter of the meat extract was regained in the form of amino-acids. Of these, glutamic acid was present in largest amount; besides those mentioned above, *iso*leucine and aspartic acid were also isolated. Similar products were obtained on directly esterifying the meat extract. E. F. A.

Proteid Reactions attributed to Tryptophan. Franz Bardachzi (*Zeit. physiol. Chem.*, 1906, **48**, 145—159. Compare Hopkins and Cole, Abstr., 1901, i, 310).—The coloured solutions obtained by treating tryptophan with "active" ether and dissolving in hydrochloric acid have been examined by means of a Hüfner spectrophotometer and the light extinction curves drawn. Different solutions give similar curves, but of varying intensity, the variations depending to a certain extent on the amount of ether used.

Solutions obtained by dissolving tryptophan in hydrochloric acid mixed with dilute glyoxylic acid have been examined similarly. When kept, these solutions become paler, but yield practically the same photometric curve. The effect of warming, however, is to force the extinction towards the blue end of the spectrum; but when a further quantity of glyoxylic acid is added to the cooled solution, the original colour and extinction are restored.

Solutions of tryptophan in hydrochloric acid and furfuraldehyde rapidly darken and cannot be examined in the same way.

Various proteids, such as ovalbumin, casein, &c., have been experimented with in the same manner as tryptophan; the clear, coloured solutions are usually obtained on warming only. The colorations are somewhat similar to those given by tryptophan, but the extinction curves are quite different.

The solutions obtained by dissolving cholic acid in fuming hydrochloric acid and furfuraldehyde and in hydrochloric acid and sucrose (2 per cent.) give curves which do not resemble one another.

J. J. S.

Photographic Determination of the Absorption Bands of the Colouring Matters of Blood. Louis Lewin, A. Miethe, and E. Stenger (*Compt. rend.*, 1906, **143**, 115—117).—The absorption spectra of blood, of hæmoglobin, and of some of its derivatives have been photographed and measured in terms of wave-lengths. From a large number of experiments with solutions of different concentrations, the most suitable dilution for the measurement of a particular band has been determined. The detailed results are summarised in a table. It appears that the absorption bands in the less refrangible part of the spectrum are in general less characteristic than those in the more refrangible portion. H. M. D.

Formation of Methæmoglobin. I. ALLEXIS BABEL (*Arch. Sci. phys. nat.*, 1906, [iv], **22**, 146—162).—The author has examined, spectroscopically, the action on pig's blood of a number of simple organic compounds, such as aniline and phenol and their principal derivatives, in order to determine their relative capacities for converting oxyhæmoglobin into methæmoglobin. Numbers are given expressing the minimum quantities in grams of the various substances required to produce an absorption band of a certain intensity when allowed to act for three hours at 20° on 20 c.c. of blood diluted to a concentration of about 5 per cent.

The methæmoglobinising activities of the substances examined are analogous to their chemical reactivities. All causes tending to render the molecule of a compound more stable, and so to diminish its capability of combination, exert influences in the same sense on the formation of methæmoglobin. Thus, the introduction of a sulphonic or carboxyl group into a molecule renders it much more resistant to the action of reagents; the sulphanilates and anthranilates have also much less marked hæmoglobinising actions than aniline, from which they are derived. T. H. P.

Action of Sodium Fluoride on Methæmoglobins obtained from Globin and Hæmatin. JOSEPH MOITESSIER (*Bull. Soc. chim.*, 1906, [iii], **35**, 575—576).—The author has investigated the optical effect produced by the addition of sodium fluoride to solutions of methæmoglobins synthesised from globin and hæmatin from various sources (Bertin Sans and Moitessier, Abstr., 1894, i, 216), and finds that the absorption bands are intensified and displaced as recorded by Ville and Derrien (Abstr., 1905, i, 399, 500). T. A. H.

Colouring Matter of Blood. VI. JOZEF BURACZEWSKI and LEON MARCHLEWSKI (*Zeit. physiol. Chem.*, 1906, **47**, 331—334. Compare Abstr., 1905, i, 399).—The product obtained by distilling α-methyl-β-propylmaleimide with zinc dust in an atmosphere of hydrogen condenses with diazobenzene chloride, yielding an azo-dye, the optical properties of which resemble those of the hæmopyrrolebisazo-dye. But although the hydrochloride of the latter crystallises readily, the hydrochloride of the dye from the synthetical product has not been obtained so far in a crystalline form. J. J. S.

Specific Action of Peroxydases. ROBERT CHODAT (*Ber.*, 1906, **39**, 2506—2507).—A claim for priority on behalf of Chodat and Bach as against Bach (this vol., i, 616). G. Y.

Hydrolytic Activity of Liver Histozymes and Enzymes on some Glucosides and Alkaloids. MAX GONNERMANN (*Pflüger's Archiv*, 1906, **113**, 168—197).—The action of the extract of the liver of the ox, hare, dog, horse, and fish, and a number of enzymes also of some bacilli has been investigated, using the glucosides sinigrin, arbutin, amygdalin, sapotoxin, and the alkaloids atropine, cocaine, morphine, and hydroxydimorphine as test materials. In no instance is sinigrin affected, showing the rarity of the occurrence of myrosin. Arbutin is hydrolysed by the liver extracts, by emulsin, by some bacilli, and by tyrosinase. Amygdalin is affected by the liver extracts of the ox and hare alone, also by trypsin, emulsin, and some bacilli, whilst it is hydrolysed within twenty-four hours by tyrosinase. Sapotoxin is hydrolysed by liver extracts and also by emulsin and tyrosinase. Atropine is attacked by the liver enzymes, also by pancreatin, by trypsin, and by tyrosinase. Cocaine by the histozymes, by pancreatin, trypsin, and emulsin, and by bacilli, but not by pepsin, maltase, or invertase. Morphine is only positively attacked by tyrosinase, and partially, perhaps, by the liver histozymes of the hare and the dog. All the enzymes were without action on hydroxydimorphine.

E. F. A.

Effect of Heat on Enzyme Activity. WILHELM CRAMER and A. R. BEARN (*Proc. Physiol. Soc.*, 1906, xxxvi—xxxvii; *J. Physiol.*, **34**).—Experiments with pepsin and rennin show that the presence of the enzyme inactivated by heating to 56—60° hinders, or in sufficient amount completely inhibits, the action of the active enzyme. Heating to 100° weakens or destroys their power. If enzyme action consists of the stages (1) the formation of a compound between substrate and enzyme, and (2) the breaking down of this compound, then the above results are explicable as follows: heating to 60° has not affected the first stage; the substrate which has combined with the inactivated enzyme cannot therefore take up the active enzyme, and is thus protected from its action. Heating to 100° changes the structure of the enzyme so profoundly that it can no longer combine with the substrate.

W. D. H.

Enzymes in Relation to Concentrated Electric Light. SIGVAL SCHMIDT-NIELSEN (*Beitr. chem. Physiol. Path.*, 1906, **8**, 481—483. Compare Abstr., 1905, ii, 48).—Concentrated electric light inactivates chymosin (rennin) to a very considerable extent. The same is true for its zymogen and for the anti-rennin of blood-serum. W. D. H.

Organic Chemistry.

Acetyl Chloride and Hydrochloric Acid as Reagents for distinguishing between the Various Types of Monohydric Alcohols. Louis Henry (*Bull. Acad. roy. Belg.*, 1906, 261—280).—Acetyl chloride reacts with primary or secondary alcohols, converting them quantitatively into esters of acetic acid (with evolution of hydrogen chloride), whereas tertiary alcohols under the same conditions are converted into chlorides.

These two reactions were found to take place concurrently and independently of each other when mixtures of tertiary with primary or secondary alcohols were treated with acetyl chloride.

Tertiary alcohols, except those of very high molecular weight, dissolve at once in fuming hydrochloric acid; the solution rapidly becomes turbid owing to the formation of the chloride, which rises to the surface as an oil. This change takes place in the cold, although the reaction is facilitated by warming gently. Primary or secondary alcohols, on the other hand, also dissolve in fuming hydrochloric acid, and two layers are again formed after a time, but the upper one in this case consists only of the unchanged alcohol saturated with hydrogen chloride, no esterification taking place unless the mixture is warmed.

P. H.

Application of the Principle of Partition. VI. Action of Hydrogen chloride on Propylene Oxide and Propenyl Alcohol. Arthur Michael (*Ber.*, 1906, **39**, 2785—2789. Compare this vol., i, 620).—By the action of dry hydrogen chloride in the cold on propylene oxide, a chlorohydrin is formed, which boils at 127—127·5° (corr.) under 722 mm. pressure and has a sp. gr. 1·113 at 20°/20°; allyl chloride yields a chlorohydrin, boiling at 126—126·5° (corr.) under 722 mm. pressure, and having a sp. gr. 1·115 at 20°/20°. The compound is probably therefore ω-chloro*iso*propyl alcohol, $CH_3·CH(OH)·CH_2Cl$, containing a small quantity of β-chloropropyl alcohol. The chlorohydrin from propenyl alcohol boiled at 127—127·5°, and had a sp. gr. 1·112 at 20°/20°; it also consisted mainly of ω-chloro*iso*propyl alcohol.

E. F. A.

Application of the Principle of Partition. VII. Action of Hydrogen Chloride on *iso*Butylene Oxide. Arthur Michael and Virgil L. Leighton (*Ber.*, 1906, **39**, 2789—2795. Compare preceding abstract).—By the action of dry hydrogen chloride on *iso*butylene oxide, an *iso*butylene chlorohydrin is obtained, which boils at 127—130°, and has a sp. gr. 1·0587 at 20°/20°, whereas the product $CH_2Cl·CMe_2·OH$, obtained by the addition of hypochlorous acid to *iso*butylene, boils at 128—129° and has a sp. gr. 1·0663 at 20°/20°. The *iso*butylene chlorohydrin when warmed with aqueous sodium carbonate or potassium acetate forms *iso*butaldehyde, and behaves, in fact, as if it were a mixture of one part of $CMe_2Cl·CH_2·OH$ and two parts of $CH_2Cl·CMe_2·OH$, a supposition confirmed by decomposition with phosphoric oxide, when a mixture of isomeric chloro*iso*butylenes is obtained two-thirds as great as if obtained from β-chloro*iso*butyl alcohol. E. F. A.

New Syntheses of Pentamethylethanol and of Hexamethylethane. LOUIS HENRY [with AUG. DE WAEL] (*Bull. Acad. roy. Belg.*, 1906, 352—363. Compare this vol., i, 477).—Pentamethylethanol may be prepared either by the action of magnesium methyl bromide on pinacolin or by the action of acetone on *tert.*-butyl chloride and magnesium. Hexamethylethane is obtained by acting on magnesium methyl bromide with an ethereal solution of bromopentamethylethane; the latter substance was prepared by passing hydrogen bromide into an alcoholic solution of the hydrate of pentamethylethanol,

$$2CMe_3·CMe_2·OH,H_2O.$$

Bromopentamethylethane, $CMe_3·CMe_2Br$, is a white solid which gradually becomes faintly yellow; it melts and partially decomposes in a sealed capillary tube at 143°. When heated in an open tube it volatilises; the substance has an odour of camphor, is very slightly soluble in alcohol, but dissolves readily in ether. P. H.

Action of Sodium on Esters of Fatty Acids. Preparation of Acyloins of the Type R·CO·CH(OH)·R. Mechanism of the Reaction. LOUIS BOUVEAULT and RENÉ LOCQUIN (*Bull. Soc. chim.*, 1906, [iii], **35**, 629—633, 633—636).—The first paper gives a general account of work already dealt with in Abstr., 1903, i, 597, 673, 730; 1904, i, 213, 642; 1905, i, 11, 12, 13, 560, and suggests the general name "acyloins" for the hydroxyketones of the type R·CO·CH(OH)·R produced in this reaction.

The yellow sodium derivative, eventually precipitated when ethyl acetate is treated with sodium by the general method already described (Abstr., 1905, i, 560), is converted by acetyl chloride into acetylmethylcarbinyl acetate, COMe·CHMe·OAc (van Reymenant, Abstr., 1901, i, 126), and the *diacetyl* derivative of *butene*-2 : 3-*diol*,

$$OAc·CMe\!:\!CMe·OAc,$$

which has a sp. gr. 0·950 at 0°/4° and boils at 110—115° under 29 mm. pressure. The former is produced by partial hydrolysis of the latter. From these reactions it appears that the yellow sodium derivative must have the constitution ONa·CMe:CMe·ONa, and that the formation of acyloins from esters takes place in the following steps: $2(R·CO_2Et) \longrightarrow ONa·CR\!:\!CR·ONa \longrightarrow OH·CR\!:\!CR·OH \longrightarrow R·CO·CHR·OH$. T. A. H.

Acyloins of the Fatty Series. III and IV. LOUIS BOUVEAULT and RENÉ LOCQUIN (*Bull. Soc. chim.*, 1906, [iii], **35**, 637—641, 641—643. Compare Abstr., 1905, i, 560, 572, and preceding abstract).—Propioin, COEt·CHEt·OH, boils at 72—73° under 20 mm. pressure, has sp. gr. 0·968 at 0°/4°, and polymerises slightly when distilled at atmospheric pressure (compare Anderlini, Abstr., 1896, i, 202). The *acetyl* derivative has a sp. gr. 1·001 at 0°/4° and boils at 85—96° under

17 mm. pressure. The *semicarbazone* forms small crystals, melts at 137°, and is readily soluble in water.

Butyroin, $COPr^{\alpha}\cdot CHPr^{\alpha}\cdot OH$, boils at 85° under 10 mm. pressure (compare Klinger and Schmitz, Abstr., 1891, 890). Its oxime (Abstr., 1905, i, 572, and Münchmeyer, Abstr., 1886, 350), when heated with acetic anhydride, decomposes into butyraldehyde and propyl cyanide. The *acetyl* derivative has a sp. gr. 0·9807 at 0°/4° and boils at 117—118° under 21 mm. pressure. When butyroin is heated with potassium hydroxide in water, the principal product is a mixture of the two stereoisomeric modifications of the glycol,

$$OH\cdot CHPr^{\alpha}\cdot CHPr^{\alpha}\cdot OH.$$

The dipropylglycollic acid which Klinger and Schmitz obtained from their butyroin in this reaction was probably formed by the action of the alkali on some dibutyryl present in the butyroin used. A mixture of butyroin and pyruvic acid when heated yields butyroin pyruvate and a liquid having the properties of 4-octanone. The former forms with semicarbazide a substance having the composition of a semicarbazone, less 1 mol. of water (compare Abstr., 1905, i, 572). Butyroin on heating with sulphuric acid yields *dibutyroin*, $C_{16}H_{28}O_2$, which is liquid, has sp. gr. 0·939, and boils at 155—157° under 12 mm. pressure.

*iso*Butyroin, $COPr^{\beta}\cdot CHPr^{\beta}\cdot OH$, has sp. gr. 0·931 and boils at 83° under 26 mm. pressure (compare Klinger and Basse, *loc. cit.*). The *oxime* melts at 110—111° and boils at 137° under 14 mm. pressure; a semicarbazone could not be obtained.

Hexonoin, $C_5H_{11}\cdot CO\cdot CH(OH)\cdot C_5H_{11}$, has a sp. gr. 0·910 at 0°/4°, boils at 130—132° under 8 mm. pressure, and when dehydrated by sulphuric acid yields dihexonoin, which boils at 225—230° under 10 mm. pressure (compare Abstr., 1905, i, 561, 573).

Pivaloin, $CMe_3\cdot CO\cdot CH(OH)\cdot CMe_3$, prepared by the general method from methyl pivalate, crystallises from ether in small needles, melts and sublimes at 81°, and is very stable. Like *iso*butyroin it does not yield a semicarbazone. T. A. H.

Hydrogenation of Fatty Acyloins. Preparation of *s*-Disecondary Glycols, Alcohols of the Type $OH\cdot CHR\cdot CH_2R$, and the Corresponding Ketones. LOUIS BOUVEAULT and RENÉ LOCQUIN (*Bull. Soc. chim.*, 1906, [iii], **35**, 643—646, 646—650. Compare preceding abstracts).—The reduction is effected by allowing an alcoholic solution of the acyloin to drop slowly into a flask containing large fragments of sodium. The products of the action are (1) a mixture of the two stereoisomeric modifications of the symmetric disecondary glycol of the type $OH\cdot CHR\cdot CHR\cdot OH$, and (2) a secondary alcohol of the type $CH_2R\cdot CHR\cdot OH$, the former being always produced in the larger quantity. Since both these reduction products are readily convertible into ketones of the type $RCO\cdot CH_2R$, the former by heating with dilute sulphuric acid at 180° in closed vessels and the latter by oxidation with chromic acid, these reactions furnish a means of converting acyloins almost quantitatively into these ketones, which the authors suggest might be called homoacylones, the symmetrical ketones, $R\cdot CO\cdot R$, being known as acylones. The products obtained from butyroin and hexonoin by these reactions are described in Abstr., 1905, i, 573.

When the mixture of the two stereoisomeric dodecane-$\zeta\eta$-diols are treated with phosphorus chloride or bromide, they furnish the two corresponding stereoisomeric halogen derivatives. The mixture of dichloro-derivatives boils at 115—135° under 10 mm. pressure and is scarcely affected by zinc dust in presence of alcohol, but the mixture of the dibromo-derivatives, similarly obtained, which boils at 145° under 10 mm. pressure, is readily reduced to dodecylene,

$$C_5H_{11}CH\!:\!CH\cdot C_5H_{11}.$$

The purest specimen of this obtained contained from 25 to 30 per cent. of a saturated hydrocarbon and boiled at 208—209°. T. A. H.

"Steric Hindrance" in Derivatives of Pivaloin. LOUIS BOUVEAULT and RENÉ LOCQUIN (*Bull. Soc. chim.*, 1906, [iii], **35**, 655—657).—Whilst the normal acyloins condense readily with semicarbazide, *iso*butyroin does so only with difficulty (this vol., i, 783). Further, whilst hydroxylamine readily gives dioximes with the normal α-diketones, it reacts much less readily with di*iso*butyryl. These observations indicate that the reactivity of a carbonyl group is lessened by the multiplication of methyl groups in its vicinity. This influence is at its maximum in pivaloin, $CMe_3\cdot CH(OH)\cdot CO\cdot CMe_3$, which does not form a semicarbazone (this vol., i, 783). Further, on reduction with sodium and alcohol it does not yield the corresponding glycol, but only the *monohydric alcohol*, $CMe_3\cdot CH(OH)\cdot CH_2\cdot CMe_3$, which separates from light petroleum in splendid crystals, melts at 52—53°, boils at 173—174°, sublimes readily, and is volatile in a current of steam. On oxidation with chromic acid in presence of sulphuric acid, it yields *homopivalone*, $CMe_3\cdot CO\cdot CH_2\cdot CMe_3$, an unpleasant-smelling liquid, which has a sp. gr. 0·827 at 0°/4° and boils at 163°. Even when heated with hydroxylamine hydrochloride and zinc oxide for seven hours, this ketone furnishes no oxime and similarly it yields no semicarbazone.

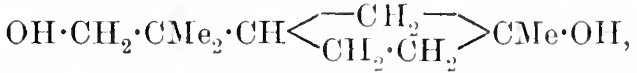
Dipivaloyl, $CMe_3\cdot CO\cdot CO\cdot CMe_3$, obtained by dehydrogenating pivaloin by Sabatier and Senderens' method, is a yellow liquid, has sp. gr. 0·895 at 0°/4°, and boils at 70° under 21 mm. and at 169—170° under atmospheric pressure. When heated with hydroxylamine hydrochloride and zinc oxide in great excess for twenty-four hours, it yields about 30 per cent. of the *monoxime*, which separates from light petroleum in slender needles and melts at 123°. T. A. H.

***tert.*-Pinacolyl Alcohol.** MAURICE DELACRE (*Bull. Acad. roy. Belg.*, 1906, 281—287).—The alcohol obtained by the action of acetone on *iso*propyl bromide and magnesium boils at 118·8—119·6° and still remains liquid at −15°, whereas the substance obtained by the reduction of pinacolin boils at 120·2—120·6° and melts at +3·6°; the synthetic compound is also more mobile. P. H.

Preparation of γ-, δ-, ϵ-, &c., Glycols and their Derivatives from the Corresponding Lactones. FRIEDRICH W. SEMMLER (*Ber.*, 1906, **39**, 2851—2857).—Good yields of γ-, δ-, &c., glycols are readily obtained by reducing the corresponding lactones with sodium and boiling alcohol. The following glycols have been prepared by this method. Pentane-*aδ*-diol from *γ*-valerolactone; a by-product is hydroxyvaleric acid. A glycol, $OH\cdot CMe_2\cdot CH<\begin{matrix}CH(CH_2\cdot OH)\\ CH_2\text{——}CH_2\end{matrix}>CHMe$ or $OH\cdot CH_2\cdot CHMe\cdot CH<\begin{matrix}CH(CH_2\cdot OH)\\ CH_2\text{——}CH_2\end{matrix}>CHMe$, from the lactone of pulegenic acid; it distils at 137—140° under 10 mm. pressure, and has n_D 1·4715 and a sp. gr. 0·9945 at 20°. With concentrated sulphuric acid, it yields an *oxide*, $C_{10}H_{18}O$. *βζ-Dimethyloctane-γθ-diol*, $OH\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH_2\cdot CH_2\cdot CH(OH)\cdot CHMe_2$, boiling at 147° under 10 mm. pressure, from the lactone of *ϵ*-hydroxy-*βζ*-dimethyloctoic acid (Baeyer, Abstr., 1900, i, 329).

o-*Hydroxydihydrocinnamyl alcohol*, $OH\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH$, a liquid distilling at 177—178° under 8 mm. pressure and having a sp. gr. 1·1293 at 20° and n_D 1·55984, is prepared from coumarin. Its *benzoyl* derivative melts at 99—100°, and with sulphuric acid the alcohol gives a good yield of chroman (Abstr., 1905, i, 294).

The compound obtained by Czerny (Abstr., 1900, i, 675) by the action of concentrated sulphuric acid on *a*-fencholenic acid (Cockburn, Trans., 1899, **75**, 506) is the lactone of *a*-fencholenic acid, and on reduction yields the corresponding *glycol*,



$$OH\cdot CH_2\cdot CMe_2\cdot CH<\begin{matrix}\text{—}CH_2\text{—}\\ CH_2\cdot CH_2\end{matrix}>CMe\cdot OH,$$

which boils at 158—161° under 11 mm. pressure. With sulphuric acid, it yields an oxide, which is identical with Wallach's fenchenol (Abstr., 1895, i, 381).

The lactone of *β*-fencholenic acid, $C_{10}H_{16}O_2$, boils at 116—118° under 8 mm. pressure, has a sp. gr. 1·0343 at 25°, and when reduced yields the *glycol*, $OH\cdot CMe_2\cdot CH<\begin{matrix}CH_2\cdot CH_2\\ \text{—}CH_2\text{—}\end{matrix}>CMe\cdot CH_2\cdot OH$, boiling at 142—143° under 8—9 mm. pressure. J. J. S.

Action of the Polyhydric Alcohols on Bismuth Salts and the Preparation of Bismuth Salts by means of a Solution of Mannitol Bismuth Nitrate. LUDWIG VANINO and F. HARTL (*J. pr. Chem.*, 1906, [ii], **74**, 142—152. Compare Vanino and Hauser, Abstr., 1902, i, 8).—On addition of much acetone to an aqueous solution of mannitol bismuth nitrate, there is formed a hard crystalline *compound*, $2Bi(NO_3)_3,C_6H_{14}O_6$, which is very soluble in water. Sorbitol and dulcitol behave towards bismuth nitrate in the same manner as does mannitol. The white, crystalline *precipitate*, $Bi(NO_3)_3,C_6H_{14}O_6$, obtained on addition of acetone to the sorbitol bismuth nitrate solution, is readily soluble in water; the similar *precipitate* obtained from the dulcitol bismuth nitrate, solution has the composition $BiO\cdot NO_3,C_6H_{14}O_6$. In aqueous solution these three substances give a blackish-brown coloration with hydrogen sulphide, do not form precipitates with potassium hydroxide, and yield bismuth oxyiodide on addition of potassium iodide.

The following salts of bismuth are prepared by adding the corresponding free acids or the sodium salts to the aqueous solution of bismuth nitrate and mannitol; a precipitate is not formed on addition of nitric acid or sodium nitrate.

Bismuth salicylate, $(OH\cdot C_6H_4\cdot CO_2)_3Bi,2H_2O$, forms a thick, white, crystalline meal, is sparingly soluble in alcohol, and on prolonged washing is converted into the basic *salt*,

$$(OH\cdot C_6H_4\cdot CO_2)_2Bi\cdot OH,(OH\cdot C_6H_4\cdot CO_2)_3Bi,2H_2O;$$

the *camphorate*, $(C_{10}H_{14}O_4)_3Bi_2,C_{10}H_{16}O_4$, is obtained as a thick, white, crystalline meal; *phthalate*, $(CO_2H\cdot C_6H_4\cdot CO_2)_3Bi$, crystallises in white, quadratic plates, and is not decomposed by potassium hydroxide; *citrate*, $OH\cdot C_3H_4(CO_2)_3Bi$, forms a white, crystalline precipitate; *benzoate*, $(C_6H_5\cdot CO_2)_3Bi$, crystallises in white needles; *oxalate*, $(C_2O_4)_3Bi_2,H_2O$, forms a white, micro-crystalline precipitate; *nitrite*, $BiO\cdot NO,\frac{1}{2}H_2O$, is obtained as a yellowish-white precipitate, which decomposes above 60° and dissolves readily in hydrochloric acid, forming a solution remaining clear on dilution; *hypophosphite*, $Bi(H_2PO_2)_3$, forms a white, crystalline precipitate, which decomposes slowly when dry, more quickly when moist, with separation of metallic bismuth; *phosphite*, $Bi_2(HPO_3)_3,3H_2O$, crystallises in white, tetragonal needles and is not decomposed by potassium hydroxide; *phosphate*, $BiPO_4,3H_2O$, forms a white, gelatinous precipitate; *borate*, $BiBO_3,2H_2O$, is obtained as a white, fine-granular precipitate, and does not react with potassium hydroxide or iodide; *ferrocyanide*, $Bi_4[Fe(CN)_6]_3,2K_4Fe(CN)_6$, forms a yellow, amorphous precipitate, which becomes green and crystalline when dried, and does not react with potassium hydroxide or iodide.

With the exceptions mentioned, these bismuth salts are blackened by hydrogen sulphide and are decomposed by potassium hydroxide and iodide. G. Y.

Compounds of Mercuric Chloride and Alcohols with Di*cyclo*pentadiene.

KARL A. HOFMANN and E. SEILER (*Ber.*, 1906, **39**, 3187—3190. Compare Hofmann and Sand, Abstr., 1900, i, 384).—The authors have investigated the action of mercuric chloride on alcoholic solutions of di*cyclo*pentadiene.

The *compound* $HgCl,C_{10}H_{12}\cdot OMe$, prepared from mercuric chloride, methyl alcohol, and di*cyclo*pentadiene, separates from a mixture of methyl alcohol and water in faintly yellow needles and melts at 133°. When acted on by hydrochloric acid, it regenerates di*cyclo*pentadiene. When its solution in concentrated sulphuric acid is warmed, it assumes a pink coloration with a green fluorescence.

The *compound* $HgCl,C_{10}H_{12}\cdot OEt$, prepared from mercuric chloride, ethyl alcohol, and di*cyclo*pentadiene, crystallises from aqueous alcohol in prisms and melts at 98°. From the stability of the compound on long exposure under diminished pressure and also at 90°, as well as from the cryoscopic determinations made in benzene solution, it is deduced that the alcohol is not present in the molecule as alcohol of crystallisation. The presence of an unsaturated linking in the molecule is shown by the behaviour of the compound towards permanganate.

The *compound* $HgCl,C_{10}H_{12}\cdot O\cdot C_5H_{11}$, obtained from amyl alcohol, mercuric chloride, and di*cyclo*pentadiene, is a heavy oil and solidifies at about −12°. A. McK.

Action of Hydrogen Bromide on Primary and Secondary Saturated Alcohols. H. Fournier (*Bull. Soc. chim.*, 1906, [iii], **35**, 621—625).—A regular current of hydrogen bromide may be obtained by allowing bromine to fall, drop by drop, into toluene containing 2 per cent. of its weight of steel wire. The hydrogen bromide so produced is passed through a reflux condenser, then through a **U**-tube containing yellow phosphorus and a little water, and finally into the appropriate alcohol contained in a flask fitted with a Vigreux column, leading to a condenser. The alcohol is at first heated to within a few degrees of its boiling point, and eventually to such a temperature that the alkyl bromide produced will just distil. The yield is always about 70 per cent.

The following alcohols have been converted into the corresponding alkyl bromides by the above method: ethyl, propyl, *iso*propyl, *iso*butyl, *n*-butyl, *n*-amyl, *iso*amyl, and *iso*hexyl. The last four alcohols were prepared by Grignard and Tissier's method (Abstr., 1902, i, 198).

T. A. H.

Organic Nitrates. Peter Klason and Tor Carlson (*Ber.*, 1906, **39**, 2752—2754).—Assuming the peroxide formula, OEt·O·NO, for ethyl nitrate (Baeyer and Villiger, *Ber.*, 1901, **34**, 755; Brühl, Abstr., 1898, ii, 362), the formation of alkali nitrate and nitrite on hydrolysis can be accounted for by means of the following reactions: OEt·O·NO + KOH = KO·O·NO + EtOH and OEt·O·NO + KOH = KO·NO + OEt·OH.

The probable formation of an alkyl peroxide has been shown by conducting the hydrolysis in the presence of phenyl hydrosulphide, when an appreciable amount of phenyl disulphide is formed, as would be expected from the equation $RO·OH + 2R'·SH = R·OH + R'_2S_2 + H_2O$. The formation of the disulphide has been proved with glyceryl trinitrate, cellulose nitrate and ethyl nitrate.

J. J. S.

Crystalline Form of Platinichlorides of Sulphine Derivatives. Gregori Aminoff (*Zeit. Kryst. Min.*, 1906, **42**, 379—383).—Crystallographic details are given respecting several substances prepared by D. Strömholm (Abstr., 1900, i, 325).

L. J. S.

Preparation of the Chloride of Methionic Acid. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 171935).—Although, as shown by Kohler (Abstr., 1898, i, 68), the action of phosphorus pentachloride on potassium methionate leads to the production of chloromethanesulphonic chloride, yet it has now been found that methionyl chloride may be prepared by treating free methionic acid with the chlorides or oxychloride of phosphorus. The dry acid (100 parts) is gently warmed with 240 parts of phosphorus pentachloride, the oxychloride distilled off, and the residue fractionated under diminished pressure. *Methionyl chloride*, $CH_2(SO_2Cl)_2$, is a colourless liquid boiling at 135° under 10 mm. pressure; it is slowly hydrolysed by water, and with aniline in chloroform solution it yields the *anilide*, $CH_2(SO_2·NHPh)_2$; this is sparingly soluble in water, but dissolves in dilute aqueous alkalis, being reprecipitated by acids.

G. T. M.

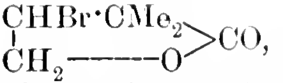
Constitution of Paris Green and its Homologues. SAMUEL AVERY (*J. Amer. Chem. Soc.*, 1906, **28**, 1155—1164).—A large number of specimens of Paris green prepared in several different ways, with an excess of copper, excess of acetic acid, excess of ammonia, or with an excess of any two of these, were analysed and found to contain between 57·3 and 57·7 per cent. of arsenious oxide [$3CuAs_2O_4,Cu(C_2H_3O_2)_2$ requires $As_2O_3 = 58·55$ per cent.]. The formic, propionic, and butyric homologues were also prepared and analysed. The results show that these substances are compounds of copper meta-arsenite and a copper salt of the organic acid combined in a ratio which is usually nearly 3 : 1, but sometimes approaches 2 : 1. Between these limits, the crystalline structure and colour do not vary with the composition. Efforts were made to obtain compounds of a ratio 4 : 1 and 1 : 1 but without success. It was found that in a series of organic acids, the stronger the acid, the more nearly does the ratio approach 3 : 1. Thus the formic acid compound is more nearly of this composition than the acetic acid compound, and the latter more so than the propionic homologue. A similar green compound can be obtained with succinic acid, and, in general, such compounds may be formed whenever an acid containing a carboxyl group yields a soluble copper salt and does not form complex ions with copper.

When Paris green of composition approximately 3 : 1 is boiled with a large excess of solution of arsenious oxide, a product of more exactly 3 : 1 composition is obtained, but the amount of arsenic never quite reaches that required by the formula $3CuAs_2O_4,Cu(C_2H_3O_2)_2$. If the boiling is continued, the substance suddenly becomes paler in colour and is converted into anhydrous copper meta-arsenite. By treating Paris green with neutral copper acetate solution, a brown, amorphous powder is obtained which contains a larger proportion of copper than Paris green and is always hydrated. When Paris green is boiled for several hours with water, it is gradually resolved into its components.

On the addition of arsenious oxide solution to a solution of zinc acetate containing a little free acetic acid, a white, granular precipitate is obtained which appears to consist of zinc meta-arsenite crystallised with a small quantity of zinc acetate. The preparation of *zinc meta-arsenite* is described. When zinc butyrate is substituted for the acetate, the precipitate obtained on adding arsenious oxide may contain as much as 10 per cent. of butyric anhydride, but in this case the precipitate contains a considerable quantity of zinc ortho-arsenite. It is evident, therefore, that the stronger acid has a greater tendency to replace arsenious acid in the zinc compounds as well as in those of copper.

E. G.

Action of Alkali Carbonates on $\beta\gamma$-Dibromo-$\alpha\alpha$-dimethyl Acids. Part I. ALFRED P. COURTOT (*Bull. Soc. chim.*, 1906, [iii], **35**, 657—664).—$\beta\gamma$-Dibromo-$\alpha\alpha$-dimethylbutyric acid is not reduced by zinc and acetic acid, but is reconverted into $\alpha\alpha$-dimethylvinylacetic acid (this vol., i, 231). On treatment with a dilute aqueous solution of potassium carbonate, it yields *β-bromo-$\alpha\alpha$-dimethylbutyrolactone*,



$\begin{array}{l}\mathrm{CHBr{\cdot}CMe_2}\\ \mid \\ \mathrm{CH_2}\text{——}\mathrm{O}\end{array}\!\!>\mathrm{CO}$, which crystallises from light petroleum in groups of colourless needles, melts at 47°, and when boiled for two hours with an aqueous solution of potassium carbonate (2 mols.) gives off carbon dioxide and yields *dimethylallyl alcohol*, $CMe_2{:}CH{\cdot}CH_2{\cdot}OH$, and *β-hydroxy-αα-dimethylbutyrolactone.* The latter crystallises in hygroscopic needles, melts at 31°, and boils at 163° under 15 mm. pressure. The formation of dimethylallyl alcohol in this reaction is assumed to take place in the following way: $CH_2Br{\cdot}CHBr{\cdot}CMe_2{\cdot}CO_2H \longrightarrow CH_2Br{\cdot}CHBr{\cdot}CHMe_2 \longrightarrow OH{\cdot}CH_2{\cdot}CH{:}CMe_2$. The alcohol is a sweet-smelling, mobile liquid, which boils at 65° under 24 mm. or at 140° under atmospheric pressure; the *acetate* is a liquid of pleasant odour and boils at 152°; the *phenylcarbamate* crystallises from a mixture of ether and light petroleum in colourless needles and melts at 65°. On bromination, dimethylallyl alcohol yields *αβ-dibromo-β-methylbutyl alcohol,* which crystallises from light petroleum in colourless needles and melts at 37—38°. On oxidation with permanganate, dimethylallyl alcohol yields acetone and oxalic acid.

When β-bromo-αα-dimethylvalerolactone is boiled with an aqueous solution of potassium carbonate (2 mols.), the products formed are the *methylpentenol,* $CMe_2{:}CH{\cdot}CHMe{\cdot}OH$, an odorous liquid, which boils at 65° under 38 mm. pressure, and *β-hydroxy-αα-dimethylvalerolactone.* The latter, which is the principal product of the reaction, separates from light petroleum in opaque crystals and melts at 80°.

The two βγ-dibromo-αα-dimethyl acids dealt with in the present paper belong to the type $R{\cdot}CHBr{\cdot}CHBr{\cdot}CMe_2{\cdot}CO_2H$, where R may be an alkyl radicle or a hydrogen atom. The acids of the type $CH_2Br{\cdot}CRBr{\cdot}CMe_2{\cdot}CO_2H$, where R may be aliphatic or aromatic, on treatment with alkali carbonates yield a tertiary alcohol, which undergoes dehydration, so that the final product of the reaction is a diethylenic hydrocarbon. It is suggested that this reaction takes place in the following steps: $CH_2Br{\cdot}CMeBr{\cdot}CMe_2{\cdot}CO_2H \longrightarrow CH_2Br{\cdot}CMe(CO_2H){\cdot}CMe_2Br \longrightarrow CH_2Br{\cdot}CHMe{\cdot}CMe_2Br \longrightarrow CH_2{:}CMe{\cdot}CMe_2Br \longrightarrow CH_2{:}CMe{\cdot}CMe_2{\cdot}OH \longrightarrow CH_2{:}CMe{\cdot}CMe{:}CH_2$.

The migration of a carboxyl group, which is assumed here, has been observed to occur in the action of phosphoric oxide on phenylhydroxypivalic acid. T. A. H.

Reaction between Silver Nitrate and Organic Halogen Compounds. HANS EULER (*Ber.*, 1906, **39**, 2726—2734. Compare J. Wislicenus, Abstr., 1882, 934; Hecht, Conrad, and Brückner, *ibid.*, 1890, 4; Wildermann, 1892, 399; Lobry de Bruyn and Steger, 1899, i, 744, 745, 849; Burke and Donnan, Trans., 1904, **85**, 555).—The reaction between monochloroacetic acid and silver nitrate, $CH_2Cl{\cdot}CO_2H + AgNO_3 + H_2O = AgCl + OH{\cdot}CH_2{\cdot}CO_2H + HNO_3$, in both aqueous and 45 per cent. alcoholic solution, is bimolecular, and the value of K for both solvents at 80° is 0·0018. The constant decreases to a slight extent as the time increases, and this is due to the formation of free nitric acid. The temperature-coefficient is relatively high, as indicated by the following numbers: 1000 K, 0·45 at 65°, 0·70 at 70°, and 1·80 at 80°.

The constant for the reaction between ethyl chloroacetate and silver nitrate in 45 per cent. alcohol is 1000 $K = 1·4$ at 85°. The constant is considerably increased when sodium chloroacetate is substituted for the free acid, as indicated by the following numbers for 1000 K. Sodium salt, 1·7 at 65°, 10·0 at 80°; acid, 0·45 at 65°, 1·80 at 80°.

When sodium nitrate is used, the constant falls to about the same value as when water alone is used. The value 1,000 K for the reaction between sodium hydroxide solution and sodium chloroacetate is 25·0 at 80° and 6·0 at 65°, and is increased by the presence of sodium chloride. The reaction between bromoacetic acid and silver nitrate, and also that between sodium bromoacetate and sodium hydroxide solution, take place more readily than in the case of the corresponding chloro-derivatives. The values for 1000 K at 65° are bromoacetic acid and silver nitrate 42, sodium bromoacetate and sodium hydroxide 195, and at 35°, ethyl bromide and silver nitrate 85, and ethyl bromide and sodium hydroxide 6·5.

The conclusions that these reactions are preceded by ionisation and the reactions measured are the rates of ionisation are adversely criticised, and the view is expressed that the reaction is due to a complex of the type $\overset{+}{Ag}\cdot C_2H_5Br$. J. J. S.

Condition of Pseudo-acids in Aqueous Solution. Heinrich Ley and Arthur Hantzsch (*Ber.*, 1906, **39**, 3149—3160).—The authors show that pseudo-acids of the class of aliphatic nitro-compounds, like nitromethane, which have practically a neutral reaction in aqueous solution, do actually, however, undergo slight electrolytic dissociation in aqueous solution; the ionisation in water is never equal to nothing, as was formerly erroneously supposed by Hantzsch and his pupils. The dissociation constant of nitromethane, as deduced from its electrical conductivity in aqueous solution, is less than that of phenol. It is now concluded that there are no abnormal relationships between the affinity constant of nitromethane and the hydrolysis of its sodium salt.

Ethyl nitroacetate, $NO_2\cdot CH_2\cdot CO_2Et$, is a pseudo-acid with a stronger tendency to ionisation than nitromethane. Its aqueous solution is distinctly acid, and it may be sharply titrated with sodium hydroxide and phenolphthalein. Determinations of its conductivity showed that it was about ten times as weak an acid as acetic acid. Solutions of its alkali salts have a distinctly alkaline reaction and are not neutral, as was formerly supposed.

Ethyl nitropropionate, $NO_2\cdot CHMe\cdot CO_2Et$, prepared by converting ethyl nitromalonate into ethyl nitro*iso*succinate and then saponifying the latter, boils at 80° under 20 mm. pressure. Its *sodium* salt crystallises in needles and melts and decomposes at 205°. Determinations of the electrical conductivity of the acid showed that in strength it is of about the same order as carbonic acid. Its sodium salt has an alkaline reaction in aqueous solution, and here again there was no evidence of abnormal hydrolysis.

Dinitroethane, which is a stronger acid than the preceding nitro-

compounds, also forms an alkali salt which undergoes appreciable hydrolysis, the degree of which is greater than that of sodium acetate.
A. McK.

Stability of Aqueous and Alcoholic Solutions of Acetic Anhydride. Auguste Lumière, Louis Lumière, and Henri Barbier (*Bull. Soc. chim.*, 1906, [iii], **35**, 625—629. Compare Abstr., 1905, i, 642).—Five and 10 per cent. solutions of the anhydride in cold water were made and set aside. From these solutions, equal aliquot parts were withdrawn every ten minutes and added to a slight known excess of aniline, which reacted quantitatively with the residual anhydride to form acetanilide. The acetic acid formed was then estimated by titration with normal sodium hydroxide solution in presence of phenolphthalein. The results are tabulated in the original, and show that the rate of hydration of the anhydride is fairly rapid at first and then decreases. It is also the more rapid the greater the initial dilution of the anhydride and the higher the temperature.

The alcoholic solutions contained (*a*) 10 per cent. of the anhydride or (*b*) alcohol and anhydride in molecular proportions, and equal aliquot portions were withdrawn at intervals of twenty-four hours and titrated with normal sodium hydroxide solution. It was observed that the amount of solution necessary to neutralise the acetic acid formed was less than the calculated quantity, unless considerable quantities of water were added before titration.

The results are tabulated in the original, and show that after a month esterification is incomplete, even in the solution initially containing anhydride and alcohol in molecular proportion. T. A. H.

Preparation of the Anhydrides of Organic Acids. Rudolf Sommer (D.R.-P. 171146).—The anhydrides of organic acids are readily prepared by heating their well-dried salts with silicon fluoride when the volatile anhydrides are distilled off from the mixture. The residue, when treated with sand and sulphuric acid, furnishes a fresh supply of silicon fluoride for the next operation. For example, silicon fluoride is passed into anhydrous sodium acetate at 200—220°, the gas is rapidly absorbed, and as this absorption ceases the acetic anhydride begins to distil over; the excess of silicon fluoride is collected in special condensing vessels. Potassium benzoate when similarly treated yields benzoic anhydride, which is extracted from the mixture with petroleum. G. T. M.

Platinous Salts of Certain Organic Acids containing Sulphur. Ludwig Ramberg (*Zeit. anorg. Chem.*, 1906, **50**, 439—445).—*Platinous xanthate*, $(OEt{\cdot}CS{\cdot}S)_2Pt$, obtained by interaction of potassium platinochloride and potassium xanthate in aqueous solution, occurs in flat, yellow prisms melting at 129—130°. It is insoluble in water, readily soluble in chloroform, and has the normal molecular weight in ethylene dibromide. It does not form additive compounds with hydrogen chloride or ammonia. *Platinous ethylthiolacetate*, $(SEt{\cdot}CH_2{\cdot}CO_2)_2Pt$, obtained by interaction of potassium ethylthiolacetate and potassium platinochloride in aqueous solution, occurs in very light green crystals. It is very soluble in boiling water, partly polymerised in glacial acetic acid solution, and combines with 1 and 2 molecules of the halogen acids to form mono- and di-basic acids respectively. It also forms an additive compound with ammonia. *Platinous phenylthiolacetate*, $(SPh{\cdot}CH_2{\cdot}CO_2)_2Pt$, obtained by interaction of sodium phenylthiolacetate and potassium platinochloride, occurs in very light green needles, melting with decomposition at 225—226°. It is slightly soluble in water, not polymerised in glacial acetic acid, forms acid additive compounds with the halogen acids, and with ammonia a compound $(SPh{\cdot}CH_2{\cdot}CO_2)_2Pt,4NH_3$, which occurs in small colourless or yellow crystals. *Platinous hydrogen thiodiglycollate*, $(CO_2H{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CO_2)_2Pt$, obtained by interaction of potassium platinochloride and potassium hydrogen thiodiglycollate or of platinous chloride and thiolacetic acid in hot concentrated aqueous solution, forms small, practically colourless needles. This compound is a dibasic acid; its acid potassium salt occurs in small, green needles.

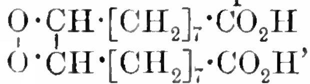
It is pointed out that the xanthate differs entirely in its behaviour from the other compounds; this is due in all probability to the presence of two sulphur atoms, one of which is joined directly to platinum. The investigation of the other three salts and their additive compounds is being continued. G. S.

Constitution of Oleic Acid and the Action of Ozone on Fats.

Ettore Molinari and E. Soncini (*Ber.*, 1906, **39**, 2735—2744. Compare Harries and Thieme, this vol., i, 227).—The iodine number 192 for the unsaturated acids obtained from pure linseed oil indicates the presence of acids containing triple linkings in addition to olefinic acids. The unsaturated acids readily combine with ozone, and the "ozone number," like the iodine number, is characteristic for each oil. The number is readily obtained by determining gravimetrically the amount of ozone absorbed by a solution of the oil in acetic acid or in a petroleum of high boiling point.

A simple method for the determination of the amount of ozone in a gaseous mixture is by absorption in olein and noting the increase in weight.

Oleic acid ozonide, $C_{18}H_{34}O_5$, is a colourless, transparent, viscous liquid, heavier than water. It does not absorb iodine and is stable up to a temperature of 80—90°. When subjected to dry distillation it yields a number of products which have not been completely investigated. When warmed with aqueous sodium hydroxide it yields a neutral product with a pleasant sharp odour and boiling at about 190°. In addition, four acids are produced, namely, *n*-nonylic acid, azealic acid, an *acid*,



$$\begin{array}{l} O{\cdot}CH{\cdot}[CH_2]_7{\cdot}CO_2H \\ O{\cdot}CH{\cdot}[CH_2]_7{\cdot}CO_2H \end{array}$$

which yields a soluble calcium salt and *a-hydroxy-a-octyldecoic* (*hydroxydioctylacetic*) *acid*, $OH{\cdot}C(C_8H_{17})_2{\cdot}CO_2H$, the calcium salt of which is insoluble in water. The last acid is a solid, waxy substance melting at about 37° and distilling at 225° under reduced pressure. The acid $C_{18}H_{32}O_6$ is an oil which decomposes when distilled under reduced pressure and may be oxidised quantitatively to azelaic acid.

The formation of these four acids is in complete harmony with the view that the double linking in the molecule of oleic acid is in the $\theta\iota$-position (compare Saytzeff, Abstr., 1893, i, 551; Baruch, Abstr., 1894, i, 170; and Lewkowitsch, *J. Soc. Chem. Ind.*, 1897, **16**, 391).
J. J. S.

Oleic Acid Ozonide. Carl D. Harries and Carl Thieme (*Ber.*, 1906, **39**, 2844—2846. Compare this vol., i, 225; Molinari and Soncini, preceding abstract).—The ozonide obtained by the action of ozone on a chloroform solution of oleic acid has the composition $C_{18}H_{34}O_6$ and is termed *oleic acid ozonide peroxide*. When purified by solution in ethyl acetate and precipitation with light petroleum, it forms a water-clear, vitreous product. When washed with water and sodium hydrogen carbonate solution, it yields the normal ozonide, $C_{18}H_{34}O_5$, which can also be prepared by the action of ozone on an acetic acid solution of oleic acid and subsequent precipitation with water and washing with the acid carbonate.

When boiled with water, the peroxide gives a much more intense hydrogen peroxide reaction than the normal ozonide. Both products yield with water, azelaic acid or its half aldehyde and nonylic acid or the corresponding aldehyde. J. J. S.

Lactonisation of $\alpha\alpha$-Dimethyl-$\beta\gamma$-unsaturated Acids. Edmond E. Blaise and Alfred P. Courtot (*Bull. Soc. chim.*, 1906, [iii], **35**, 580—588).—When $\alpha\alpha$-dimethylvinylacetic acid is dissolved in sulphuric acid and the solution is immediately poured into excess of water the principal product is β-hydroxy-$\alpha\alpha$-dimethylbutyric acid, but if the solution be warmed trimethylethylene is formed. When dimethylvinylacetic acid is treated with hydrobromic acid, the bromine atom is added on, partly in the β- and partly in the γ-position, and the product on treatment with alkali carbonates yields a mixture of trimethylethylene and $\alpha\alpha$-dimethylbutyrolactone. With hydrogen iodide, the iodine atom takes the β-position and the product on treatment with alkali carbonates yields only trimethylethylene. The latter boils at 37—38°; its *dibromide* melts at 7° and boils at 57° under 14 mm. pressure.

$\alpha\alpha$-Dimethylbutyrolactone is a liquid with a strong odour, melts at 6° and boils at 84° under 13 mm. pressure. $\alpha\alpha$-Dimethylvalerolactone, obtained by dehydrating dimethylpropenylacetic acid [mol. vol. (calc.) 138·9] with sulphuric acid, or by the action of alkali carbonates on γ-iodo-$\alpha\alpha$-dimethylvaleric acid, prepared by adding hydrogen iodide to dimethylpropenylacetic acid, crystallises from light petroleum, melts at 52°, and has the mol. vol. 130·44 at 28° (compare Blanc, Abstr., 1905, i, 680). When heated during twelve hours at 300° with an equal weight of potassium cyanide, the lactone yields potassium γ-cyano-$\alpha\alpha$-dimethylvalerate, and this is converted by hydrochloric acid into *trimethylglutarimide*, which melts at 139° and sublimes readily.

Dimethyl*iso*propenylacetic acid, when warmed with sulphuric acid, yields first hydroxytrimethylbutyric acid and then tetramethylethylene (Reformatsky and Plesconosoff, Abstr., 1896, i, 128).

β-Bromo-ααβ-trimethylbutyric acid, $CMe_2Br\cdot CMe_2\cdot CO_2H$, obtained by the action of hydrobromic acid on dimethyl*iso*propenylacetic acid, crystallises from a mixture of ether and light petroleum and decomposes at 150°. *β-Iodo-ααβ-trimethylbutyric acid*, obtained in an analogous manner, forms small crystals and decomposes at 170°. Both these halogen derivatives, when treated with alkali carbonates, yield tetramethylethylene. The latter boils at 72°. The *dibromide* separates from ether in characteristic quadratic prisms, and melts and decomposes at 92°.

Phenyldimethylvinylacetic acid is not readily attacked by hot sulphuric acid, and the sole product is *phenyltrimethylethylene*. This is a mobile liquid, boils at 83° under 12 mm. and at 189° under atmospheric pressure, yields oily products with bromine or hypochlorous acid, and on oxidation with permanganate furnishes acetone and acetophenone.

Sulphuric acid has no action on benzyldimethylvinylacetic acid. Hydroxyvinylpivalic acid, on treatment with sulphuric acid, furnishes a neutral product, which is not volatile under reduced pressure and may be a polymerised diethylenic hydrocarbon.

The foregoing results show that Fittig's rule for the diagnosis of βγ-unsaturated acids is not quite generally applicable. Acids of the type $CHR\colon CH\cdot CMe_2\cdot CO_2H$ readily yield lactones under these conditions, whilst acids of the type $CH_2\colon CR\cdot CMe_2\cdot CO_2H$ furnish first the corresponding hydroxypivalic acids, and these are then decomposed into carbon dioxide and the unsaturated hydrocarbons. Acids of this class containing an aromatic nucleus are either unattacked by sulphuric acid, or yield a small quantity of the corresponding unsaturated hydrocarbon. T. A. H.

Abnormal Dehydration of Hydroxyalkylpivalic Esters. II.

EDMOND E. BLAISE and ALFRED P. COURTOT (*Bull. Soc. chim.*, 1906, [iii], **35**, 589—600. Compare Abstr., 1905, i, 853, and this vol., i, 553).—When ethyl hydroxypivalate (ethyl β-hydroxy-αα-dimethylpropionate) is dehydrated by means of phosphoric oxide, a mixture of ethyl tiglate and ethyl angelate is produced, the former preponderating. A portion of the ethyl tiglate is attacked by the phosphoric acid, yielding ethylene and tiglic acid, whilst the ethyl hydroxypivalate is also partially hydrolysed, and the acid liberated is decomposed, yielding hemipolylactide.

Ethyl phenylhydroxypivalate (ethyl β-phenyl-αα-dimethylhydracrylate), on treatment with phosphoric oxide, yields ethyl dimethylatropate (ethyl α-phenyl-ββ-dimethylacrylate) as a principal product, with small quantities of ethyl *iso*butyrate, *phenyl dimethylethylene*, $CMe_2\colon CHPh$, which boils at 72° under 15 mm. pressure, and yields an oily *dibromide*, and benzaldehyde (the semicarbazide of the latter melts at 235°; compare Thiele and Stange, Abstr., 1895, i, 251).

Dimethylatropic acid, $CMe_2\colon CPh\cdot CO_2H$, separates from warm alcohol in brilliant needles and melts at 151°; the *methyl* ester forms prismatic crystals, melts at 32°, and boils at 142° under 26 mm. pressure;

the *ethyl* ester is a mobile liquid and boils at 136° under 17 mm. pressure. When treated with bromine in carbon disulphide, the acid furnishes *αβ-dibromo-α-phenyl-β-methylbutyric acid*, which crystallises from light petroleum in needles and melts at 105°. Ethyl dimethylatropate, on reduction with sodium, yields *α-phenyl-β-methylbutyl alcohol*, $CHMe_2 \cdot CHPh \cdot CH_2 \cdot OH$, a viscous liquid with a thyme-like odour, and boiling at 127° under 15 mm. pressure; the *acetate* is a mobile, pleasant-smelling liquid, and boils at 134° under 15 mm. pressure. On oxidation with permanganate in presence of potassium hydrogen carbonate, dimethylatropic acid yields acetone and a mixture of benzoic and phenylglycollic acids.

Ethyl dimethyltropate is obtained, together with some ethyl-αα-diphenylsuccinate, by condensing acetone with ethyl phenylbromoacetate in presence of zinc. It is a viscous liquid and boils at 152° under 19 mm. pressure. On hydrolysis with potassium hydroxide in alcohol, it furnishes no dimethyltropic acid, but only acetone and phenylacetic acid, and on treatment with phosphoric oxide yields ethyl dimethylatropate, identical with that obtained by the dehydration of ethyl phenylhydroxypivalate (see above).

When benzophenone is condensed with ethyl bromo*iso*butyrate, a very small quantity of *ethyl β-hydroxy-ββ-diphenylpivalate*,

$$OH \cdot CPh_2 \cdot CMe_2 \cdot CO_2Et,$$

is formed. This crystallises from light petroleum in superb needles and melts at 101°.

*Ethyl benzoyl*iso*butyrate*, $CMe_2Bz \cdot CO_2Et$, obtained by condensing benzonitrile with ethyl bromo*iso*butyrate in presence of zinc (Abstr., 1901, i, 252), is a slightly mobile liquid and boils at 152° under 20 mm. pressure. When condensed with bromobenzene in presence of zinc, no ethyl diphenylhydroxypivalate is formed.

Benzophenone semicarbazone crystallises from warm alcohol in small needles and melts at 167°. T. A. H.

A New Case of Tautomerism. LUDWIG KNORR and WILLIAM HICKS (*Ber.*, 1906, **39**, 3255—3257).—Ethyl thioacetoacetate (compare Buchka, Abstr., 1890, 28; Michaelis and Philipps, *ibid.*, 582) in alcoholic or benzene solution is converted rapidly into the enolic isomeride, $S[C(CO_2Et){:}CMe \cdot OH]_2$, which is obtained best by keeping overnight an ethereal solution of the ester containing a trace of sodium hydroxide. It is a transparent oil which passes, slowly of itself, rapidly by shaking with sodium carbonate solution, into the solid ketonic modification. C. S.

Anhydrides of Dibasic Acids. GERARDUS L. VOERMAN (*Bull. Soc. chim.*, 1906, [iii], **35**, 665—666).—It is stated that Blaise and Houillon in a note recently published (*Bull. Soc. chim.*, 1906, [iii], **35**, 199) have given the impression that the author's work (Abstr., 1904, i, 287; 1905, i, 13) on the molecular weights of the anhydrides of the dibasic acids showed that these substances were unimolecular, whereas it was shown that, although cryoscopic determinations in phenol gave normal results, ebullioscopic measurements in acetone gave results indicating that the anhydrides of the acids above adipic acid are polymerised. T. A. H.

Anhydrides of Dibasic Acids. EDMOND E. BLAISE (*Bull. Soc. chim.*, 1906, [iii], **35**, 666).—A reply to Voerman (see preceding abstract), in which a detailed consideration of the latter's results is promised in a forthcoming paper on the anhydrides of dibasic acids.

T. A. H.

Decomposition of Malonic Ester Chloride. HERMANN LEUCHS (*Ber.*, 1906, **39**, 2641—2643).—The author has shown previously that when carbethoxyglycyl chloride is heated, it forms glycinecarboxylic anhydride with elimination of methyl chloride (this vol., i, 236). Ethyl malonate chloride has now been studied from the same standpoint.

When ethyl malonate chloride was heated for one hour at 125—130°, hydrogen chloride was evolved, but there was no evidence of the formation of ethyl chloride. The residue yielded the *compound* $C_{13}H_{12}O_8$, which separated from methyl alcohol in yellow prisms and melted at 170—180° (corr.). A determination of its molecular weight by the cryoscopic method in benzene solution gave a value corresponding with the formula quoted.

From methyl malonate chloride, the corresponding methyl *compound*, $C_{11}H_8O_8$, is formed in an analogous manner. It melts at 184—185° (corr.), and is similar in behaviour to the ethyl compound.

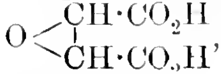
A. McK.

Halogenated Aliphatic Acids. II. WILHELM LOSSEN (*Annalen*, 1906, **348**, 261—346. Compare Abstr., 1893, i, 142, and this vol., i, 59).—[With ERICH MENDTHAL.]—The velocity of the conversion of bromosuccinic acid into fumaric acid in the presence of water and at various concentrations (1—3 mol. proportions) has been investigated. The reaction is greatly accelerated by the presence of an alkali hydroxide, even when the solution remained acid after the addition of 1 mol. of the base. From a consideration of the possible configurations of the salts of bromosuccinic acid, it is concluded that the sodium hydrogen salt alone undergoes this decomposition.

[With WALTHER BERGAU.]—Tribromosuccinic acid, prepared by a modification of Petri's method (Abstr., 1879, 373), crystallises in plates melting at 136° and is not hygroscopic; its *aniline* salt, prepared by mixing the ethereal or alcoholic solutions of its constituents, crystallises in prisms. An aqueous solution of the acid is decomposed quantitatively into dibromoacrylic acid, carbon dioxide, and hydrogen bromide. One hundred parts of a saturated solution of dibromoacrylic acid at 90° contains 8·2 parts of the acid.

When tribromosuccinic acid is treated with potassium hydroxide, it is converted quantitatively into dibromomaleic acid, provided that 3 mols. of the base are used for each mol. of the acid. On allowing gaseous ammonia to come in contact with a highly concentrated aqueous solution of tribromosuccinic acid, dibromomaleic acid is also produced, but if the acid is treated with strong aqueous ammonia, bromofumaric acid is formed. If a solution of tribromosuccinic acid in benzene is boiled, dibromomaleic acid is alone formed, a fact which is not in agreement either with Wislicenus's experimental results or his theoretical views.

[With Walther Schörk and Max Niehrenheim.]—*Chloromalic acid*, $CO_2H·CHCl·CH(OH)·CO_2H$, is readily prepared from either sodium maleate or fumarate by adding chlorine water to the aqueous solution of the salt: $C_4H_2O_4Na_2 + Cl_2 + H_2O = C_4H_4O_5ClNa + NaCl$. The acid crystallises in monoclinic needles [$a : b : c = 1·387 : 1 : 0·84904$; $\beta = 65°41'$] melting at 143° and decomposing at a somewhat higher temperature. The *sodium* and *silver* salts are anhydrous, whilst the *barium* salt crystallises with $3H_2O$, and the *lead* salt with $2H_2O$. The *methyl* ester is an oily liquid. When subjected to dry distillation, chloromalic acid is mainly converted into chloromaleic acid, the same compound being also formed on heating the acid with a saturated solution of hydrochloric acid under pressure. On reduction with a zinc platinum couple in aqueous solution, malic acid is formed. When the aqueous solution is boiled, carbon dioxide, aldehyde, and hydrochloric and tartaric acids are produced, the rate of the decomposition increasing with the dilution: $C_4H_5O_5Cl + H_2O = C_4H_6O_6 + HCl$; $C_4H_5O_5Cl = C_2H_4O + CO_2 + HCl$. A similar decomposition occurs when potassium hydrogen chloromalate is boiled in aqueous solution. The normal salt decomposes in a similar manner, but the main reaction is the formation of aldehyde and carbon dioxide. When boiled with an excess (3 mols.) of *N*-potassium hydroxide, a reaction takes place quantitatively according to the following equation: $C_4H_5O_5Cl + 3KOH = C_4H_4O_6K_2 + KCl + 3H_2O$, *fumarylglycidic acid*,

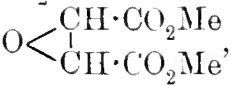


being produced.

[With Hans Dueck and Max Leopold.]—*Bromomalic acid*,

$$CO_2H·CHBr·CH(OH)·CO_2H,$$

is prepared by the action of bromine water on an alkaline solution of fumaric acid; the acid forms monoclinic crystals, isomorphous with chloromalic acid and melting at 132—134°. The *sodium* salt is anhydrous and decomposes at 100°; the *barium* salt crystallises with 3 and $4H_2O$, whilst the *lead* and *silver* salts are anhydrous. When subjected to dry distillation, carbon dioxide, hydrogen bromide, and bromomaleic acid are formed. If the aqueous solution is boiled, carbon dioxide, aldehyde, and hydrobromic and racemic acids are produced, whilst, as in the case of chloromalic acid, the action of sodium hydroxide leads quantitatively to the formation of fumarylglycidic acid. When an attempt was made to prepare this acid from barium maleate, a bromomalic acid was obtained, which crystallised with H_2O and melted at 63—65°; its salts are identical with those of the anhydrous acid, and on melting it yields the crystals of the latter. If a solution of molecular proportions of the anhydrous acid and water are made in ether or chloroform, the anhydrous acid crystallises out on evaporation, but if the solution is sown with a crystal of the hydrated acid, the latter separates. The decomposition of the hydrated acid in water is similar to that of the anhydrous, but it was found that mesotartaric acid was formed at the same time as racemic acid. The barium salts of both acids behaved in a similar manner when their solutions were boiled. Both acids were converted into fumarylglycidic acid with equal ease.

[With Walther Schörk, Max Niehrenheim, Hans Dueck, and Max Leopold.]—Fumarylglycidic acid, prepared either from chloro- or bromo-malic acid, forms prismatic crystals melting at 203°; its *sodium* salt, $C_4H_3O_5Na,H_2O$, crystallises in plates, the *calcium*, *barium*, and the *lead* salts each crystallise with $2H_2O$, whilst the *silver* salt is anhydrous and explosive. The *methyl* ester,  $O<\begin{matrix}CH\cdot CO_2Me\\ |\\ CH\cdot CO_2Me\end{matrix}$, prepared from the silver salt and methyl iodide, crystallises in needles melting at 73°, and reacts neither with acetyl chloride nor with phenylcarbimide; hence no hydroxyl group is present. The *acid chloride*, prepared from the acid and phosphorus pentachloride, forms scaly crystals melting at 53° and boiling at 90—93° under 40 mm. pressure. The *diphenyl ester*, $C_2H_2O(CO_2Ph)_2$, prepared from the acid chloride and phenol, forms crystals melting at 133°. The *amide*, $C_2H_2O(CO\cdot NH_2)_2$, prepared from the methyl ester and alcoholic ammonia, is a microcrystalline solid melting and decomposing at 225°.

On boiling the fumarylglycidic acid with water, carbon dioxide, aldehyde, and racemic and mesotartaric acids are formed. Concentrated hydrochloric and hydrobromic acids convert the acid into the corresponding halogen malic acids; with ammonia, it combines to form aminomalic acid.

[With Erich Mendthal.]—When aqueous solutions of bromofumaric or bromomaleic acids are boiled, they are decomposed into carbon dioxide, aldehyde, and propargylic acid. A similar decomposition occurs if the normal sodium or sodium hydrogen salts are heated in aqueous solution, but in the presence of excess of alkali hydroxide, on the other hand, acetylenedicarboxylic acid is the main product, a portion afterwards decomposing into propargylic acid. Under all conditions, bromofumaric acid decomposes more rapidly than bromomaleic acid; the normal salts decompose most readily, whilst the free acids and the hydrogen salts are relatively stable.

On reducing either of the acids with sodium amalgam or with zinc, fumaric and succinic acids are produced.

[With Adolf Treibich.]—Anhydrous acetylenedicarboxylic acid is prepared by treating the ethereal solution of the hydrated acid with calcium chloride. When a concentrated aqueous solution of the acid is treated with the calculated quantity of bromine vapour, it is converted quantitatively into dibromofumaric acid together with a small quantity of dibromomaleic acid. Acetylenedicarboxylic acid is easily oxidised by permanganate to oxalic acid and carbon dioxide.

The action of bromine on a dilute aqueous solution of acetylenedicarboxylic acid is very complicated, and is represented by the following equations: $C_4H_2O_4 + 4H_2O + 5Br_2 = 4CO_2 + 10HBr$; $C_4H_2O_4 + 4H_2O + 3Br_2 = 2C_2H_2O_4 + 6HBr$; $C_4H_2O_4 + HBr = C_4H_3O_4Br$; $C_4H_2O_4 + Br_2 = C_4H_2O_4Br_2$.

[With Walther Bergau.]—The action of chlorine on acetylenedicarboxylic acid and of chlorine or bromine on sodium acetylenedicarboxylate was investigated under various conditions, but in no case was a simple reaction observed. K. J. P. O.

Preparation of Peroxide Acids from the Anhydrides of Dibasic Acids. FREDERICK STEARNS & CO. (D.R.-P. 170727).—Peroxide acids having pronounced antiseptic and germicidal properties are produced on shaking the anhydrides of the dibasic acids with a dilute aqueous solution of hydrogen peroxide until a precipitate is produced. Peroxide-phthalic acid, a substance already described, can be prepared in this way, and the reaction takes place equally readily with succinic and glutaric anhydrides.

Peroxide succinic acid, $O_2(CO\cdot CH_2\cdot CH_2\cdot CO_2H)_2$, separates in colourless tabular crystals slightly soluble in water, alcohol, ethyl acetate, acetic acid, or ether, and insoluble in chloroform or benzene. Water slowly hydrolyses it, yielding molecular proportions of succinic acid and succinic peracid, $CO_2H\cdot CH_2\cdot CH_2\cdot CO\cdot O\cdot OH$.

Peroxide glutaric acid, $O_2(CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CO_2H)_2$, is prepared similarly by shaking glutaric anhydride for half an hour with 7·8 per cent. aqueous hydrogen peroxide at 30°. G. T. M.

Solubility of Alkaline Earth Malates in Water. H. CANTONI and M. BASADONNA (*Bull. Soc. chim.*, 1906, [iii], **35**, 727—737. Compare Abstr., 1904, i, 142).—Strontium malate is the most soluble of the three salts and its solubility increases greatly with rise of temperature. The least soluble salt is calcium malate, and its solubility diminishes as the temperature is increased. The solubility of barium malate is intermediate between that of the calcium and strontium salts and increases very slightly with rise of temperature. The experimental results are tabulated in detail in the original, which also gives a number of solubility curves for the three salts, and details of the methods employed in conducting the experiments and in estimating malic acid. T. A. H.

Increase and Reversal of Rotation. I. Complex Molybdyl and Tungstyl Malates. HERMANN GROSSMANN and HEINZ PÖTTER (*Zeit. physikal. Chem.*, 1906, **56**, 577—604. Compare this vol., ii, 211; also Itzig, Abstr., 1901, i, 580).—The rotatory power of solutions containing malic acid and ammonium molybdate, sodium molybdate, or sodium tungstate varies often in a peculiar manner when the concentration and the temperature are altered. The authors have made an extensive study of these variations, their measurements covering the following molecular combinations: (1) 1 mol. $C_4H_6O_5 + 0·5$ mol. $(NH_4)_2MoO_4$ (compare Grossmann and Pötter, Abstr., 1904, ii, 153); (2) 1 mol. $C_4H_6O_5 + 0·5$ mol. Na_2MoO_4; (3) 1 mol. $C_4H_6O_5 + 1$ mol. Na_2MoO_4; (4) 1 mol. $C_4H_6O_5 + 1·5$ mols. Na_2MoO_4; (5) 1 mol. $C_4H_6O_5 + 2$ mols. Na_2MoO_4; (6) 1 mol. $C_4H_6O_5 + 4$ mols. Na_2MoO_4; (7) 1 mol. $C_4H_6O_5 + 1$ mol. $Na_2MoO_4 + 1$ mol. MoO_3; (8) 1 mol. $C_4H_6O_5 + 0·5$ mol. Na_2WO_4; (9) 1 mol. $C_4H_6O_5 + 1$ mol. Na_2WO_4; (10) 1 mol. $C_4H_6O_5 + 1·5$ mols. Na_2WO_4; (11) 1 mol. $C_4H_6O_5 + 2$ mols. Na_2WO_4. The observations indicate that the peculiar variations of rotation are in some cases due to the formation of molybdyl and tungstyl dimalates, which are highly active complexes and are but slightly affected by changes of concentration and temperature. In other cases molybdyl and tungstyl malates are formed, the formulæ of the complexes being probably

$CO_2Na\cdot CH_2\cdot CH(OH)\cdot CO\cdot O\cdot MoO_2\cdot ONa$ and
$CO_2Na\cdot CH_2\cdot CH(OH)\cdot CO\cdot O\cdot WO_2\cdot ONa$.

The rotation of the molybdyl malate is at the ordinary temperature but little affected by change of concentration, but with rise of temperature it decreases regularly and markedly at all concentrations. In the case of the tungstyl malate, dilution and rise of temperature both produce a marked increase in rotation. When 1 molecule of malic acid is mixed with more than 1 molecule of sodium molybdate or tungstate, complexes are formed, which are sometimes dextrorotatory, sometimes lævorotatory, and which are very sensitive to changes of concentration and temperature. The molybdyl complexes of this kind appear to be completely resolved at high dilution into the 1 : 1 salt and inactive sodium molybdate: this splitting up of the higher complex is not quite so definite in the case of the tungstyl compounds. That so many cases of maxima, minima, and reversal of rotation have been observed by the authors is probably due to the formation in the concentrated solutions of slightly stable additive products, characterised by rotations of opposite sign. J. C. P.

Preparation of Mercury Cholates. J. D. Riedel (D.R.-P. 171485).—Mercury cholates are not easily obtained by the double decomposition between cholic acid and the inorganic mercury salts, for in these cases the product is either colloidal or contains excess of the corresponding mercury oxide. Either mercurous or mercuric cholate may, however, be produced readily by employing the mercury salt of an organic acid such as acetic acid. A 5 to 10 per cent. aqueous solution of a soluble cholate is introduced, with vigorous stirring, into a solution of mercurous or mercuric acetate, when the corresponding mercury salt is deposited as a yellowish-white precipitate which can be readily collected and dried.

Mercurous cholate, $C_{24}H_{39}O_5Hg$, is a yellowish-white, insoluble powder, decomposed by alkalis or alcohol. *Mercuric cholate*, $(C_{24}H_{39}O_5)_2Hg$, is similar in appearance, but rather more soluble, particularly in acidified water or in aqueous solutions of sodium or potassium chloride; it is also decomposed by alcohol. G. T. M.

New Derivatives of δ-Ketonic Acids. Icilio Guareschi (*Atti R. Accad. Sci. Torino*, 1906, **41**, 842—861. Compare Abstr., 1898, i, 274; 1900, i, 52, 111; 1901, i, 341, 630; 1902, i, 819; 1903, i, 736; 1905, i, 821).—The interaction of molecular proportions of ethyl acetoacetate, ethyl cyanoacetate, and *n*-butaldehyde in presence of ammonia yields the ammonium derivative of propyldicyanodioxypyridine (Abstr., 1902, i, 819) and *γ-carbethoxy-γ-acetyl-β-propylbutyronitrile-α-amide*, $CO_2Et\cdot CHAc\cdot CHPr\cdot CH(CN)\cdot CO\cdot NH_2$, which crystallises from water in shining, colourless prisms, melts at 205—206°, and dissolves in alcohol or acetic acid. It has a neutral reaction, does not absorb bromine and is soluble in sodium hydroxide solution with evolution of ammonia. When heated with excess of barium hydroxide solution, it yields 2 mols. of ammonia and γ-carbethoxy-γ-acetyl-β-propylbutyric acid (?), which forms a soluble barium salt. On heating with hydrochloric acid of sp. gr. 1·19, it yields *γ-carbethoxy-γ-acetyl-β-propylbutyronitrile*,

$$CO_2Et\cdot CHAc\cdot CHPr\cdot CH_2\cdot CN,$$

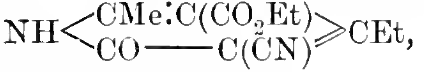
which crystallises from water in long, colourless needles, or from alcohol in prisms, melts at 125—126°, has a neutral reaction, and reduces permanganate. When heated with 60 per cent. sulphuric acid, it gives γ-carbethoxy-γ-acetyl-β-propylbutyric acid (?).

If the ethyl acetoacetate employed in the above reaction is replaced by the corresponding methyl ester, there is obtained *γ-carbmethoxy-γ-acetyl-β-propylbutyronitrile-α-amide*,

$$CO_2Me\cdot CHAc\cdot CHPr\cdot CH(CN)\cdot CO\cdot NH_2,$$

which separates from water in crystals melting at 248—249°.

When mixed in molecular proportions, propaldehyde, ethyl acetoacetate, and ethyl cyanoacetate in presence of ammonia yield (1) the ammonium derivative of dicyanodioxyethylpyridine, (2) a compound which is probably



$NH<\begin{matrix}CMe\colon C(CO_2Et)\\ CO\text{———}C(CN)\end{matrix}>CEt$, and (3) *γ-carbethoxy-γ-acetyl-β-ethylbutyronitrile-α-amide*,

$$CO_2Et\cdot CHAc\cdot CHEt\cdot CH(CN)\cdot CO\cdot NH_2,$$

which separates from water in crystals melting at 199—200°, and, on boiling with hydrochloric acid, yields *γ-carbethoxy-γ-acetyl-β-ethylbutyronitrile* (?), $CO_2Et\cdot CHAc\cdot CHEt\cdot CH_2\cdot CN$, crystallising from water in long needles melting at 92—94°, and dissolving in ether or alcohol.

Acetaldehyde, ethyl acetoacetate, ethyl cyanoacetate and ammonia yield methyldicyanoglutaconimide, ethyl hydrocollidinedicarboxylate, and *γ-carbethoxy-γ-acetyl-β-methylbutyronitrile-α-amide*,

$$CO_2Et\cdot CHAc\cdot CHMe\cdot CH(CN)\cdot CO\cdot NH_2,$$

which melts at 212—213° and is soluble in alcohol or water.

γ-Carbethoxy-γ-acetyl-β-phenylbutyronitrile-α-amide,

$$CO_2Et\cdot CHAc\cdot CHPh\cdot CH(CN)\cdot CO\cdot NH_2,$$

obtained with other products by the interaction of benzaldehyde, ethyl acetoacetate, methyl or ethyl cyanoacetate, and ammonia, crystallises from alcohol in shining, acicular prisms melting at 225—226° and exhibits characters resembling those of the corresponding compounds prepared from aliphatic aldehydes. When heated with hydrochloric acid of sp. gr. 1·19 in presence of alcohol, it yields *γ-carbethoxy-γ-acetyl-β-phenylbutyronitrile*, which melts at 152—154° and is soluble in ether.

γ-Carbmethoxy-γ acetyl-β-phenylbutyronitrile-α-amide,

$$CO_2Me\cdot CHAc\cdot CHPh\cdot CH(CN)\cdot CO\cdot NH_2,$$

forms heavy, colourless crystals melting at 234—235° and dissolves in water or alcohol.

The interaction of formaldehyde, ethyl acetoacetate, and ethyl cyanoacetate in presence of ammonia yields only a small proportion of *γ-carbethoxy-γ-acetylbutyronitrile-α-amide*,

$$CO_2Et\cdot CHAc\cdot CH_2\cdot CH(CN)\cdot CO\cdot NH_2,$$

which crystallises in short, heavy prisms melting at 178—180°, the main product being a dicyano-pyridine derivative. T. H. P.

Synthetical Experiments with *d*-Gluconic Acid. II. Carl Paal and Franz Hörnstein (*Ber.*, 1906, 39, 2823—2827. Compare this vol., i, 400).—The lactone of tetra-acetyl-*d*-gluconic acid is obtained as a transparent, faintly yellow-coloured, gummy mass, giving correct results on analysis if care be taken to avoid the use of alcohol in isolating it. It is sparingly soluble in hot water and in benzene solution has $[\alpha]_D$ + 70·86° at 21°. The experimental methods have been improved so as to prepare 1 : 1-diphenyl-*d*-sorbitol in a crystalline form melting at 157—160°; the cold supersaturated solutions in water and alcohol have $[\alpha]_D$ + 71·25° and + 74·75° respectively at 25°.

E. F. A.

Synthetical Experiments with *d*-Galactonic Acid. Carl Paal and Erich Weidenkaff (*Ber.*, 1906, 39, 2827—2833. See preceding abstract).—*Tetra-acetyl*-d-*galactonic lactone*, prepared by heating the lactone with acetic anhydride, is obtained as a transparent, tough gum having $[\alpha]_D$ − 1·04° at 20°; the product obtained by acetylating at 50—60° has $[\alpha]_D$ − 8·5° at 20°. 1 : 1-*Diphenyl*-d-*galactohexitol*, obtained by heating the acetyl-lactone, dissolved in benzene, with magnesium phenyl bromide crystallises in ball-like aggregates of colourless, faintly-glistening needles melting at 157—160° and containing H_2O. It is less soluble in water and more so in alcohol than diphenylsorbitol. The supersaturated solution in water has $[\alpha]_D$ + 72·9° at 20°, and in alcohol $[\alpha]_D$ + 56·23° at 20°. A by-product of the action of magnesium phenyl bromide is described melting at 93—97° and yielding, when heated with potassium hydroxide, crystals melting at 98—100° which show $[\alpha]_D$ − 106·4° at 20°.

E. F. A.

Physiological Relationships of the Proteids containing Sulphur. IV. Ernst Friedmann and Julius Baer (*Beitr. chem. Physiol. Path.*, 1906, 8, 326—331. Compare Abstr., 1902, i, 731; 1903, i, 75, 301; 1904, i, 165).—A specimen of pure proteid cystein or α-amino-β-thiolactic acid disulphide, when heated in the form of its hydrochloride with water at 145° for 1·5 hours and then reduced with tin and hydrochloric acid, yields α-thiolactic acid. The formation of this acid is not due, as suggested by Mörner (Abstr., 1904, i, 836), to the presence of an isomeric cystein in the natural product, but is formed from the pure disulphide of α-amino-β-thiolactic acid, probably through the intermediate formation of pyruvic acid, as this is known to yield a product with hydrogen sulphide which on reduction gives α-thiolactic acid.

J. J. S.

Zinc Formaldehydesulphoxylate. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 172217).—Sodium formaldehydesulphoxylate was formerly isolated by the fractional crystallisation from the other substances produced by the interaction of formaldehyde and sodium hyposulphite. It is now found that formaldehydesulphoxylic acid forms a sparingly soluble zinc salt which is readily separated from the sulphide present. The separation is best effected by treating a solution of zinc formaldehydehyposulphite with sodium carbonate in accordance with the following equation: $2ZnS_2O_4,2CH_2O$

$+ \mathrm{Na_2CO_3} + \mathrm{3H_2O} = \mathrm{2ZnSO_2,CH_2O,H_2O} + \mathrm{2NaHSO_3,CH_2O} + \mathrm{CO_2}$. A solution of zinc hyposulphite, $\mathrm{ZnS_2O_4}$ (100 grams) is treated with formaldehyde until it loses its power of reducing indigotinsulphonic acid in the cold, and then 25 grams of dry sodium carbonate are added. The new zinc salt, which separates slowly, is washed and dried; it is a crystalline substance which is stable in the air and which, on digestion with aqueous sodium carbonate, yields a solution of sodium formaldehydesulphoxylate. G. T. M.

Condensation of Tiglic Aldehyde with Acetone. FRITZ DAUTWITZ (*Monatsh.*, 1906, **27**, 773—776).—Tiglic aldehyde, prepared by heating a mixture of acetaldehyde and propaldehyde with sodium acetate solution, condenses with acetone in aqueous sodium hydroxide solution at 5—10°, forming an unsaturated *ketone*,

$$\mathrm{CHMe{:}CMe{\cdot}CH{:}CH{\cdot}COMe},$$

which is obtained as a colourless, strongly refracting, mobile oil. It has a characteristic aromatic odour, boils at 92—93° under 12 mm. pressure, is rapidly oxidised by air forming a resin, and forms an *additive* compound with 2 mols. of bromine. The *oxime*, $\mathrm{C_{18}H_{13}ON}$, crystallises from light petroleum and melts at 71°, forming a viscid, colourless, strongly refracting oil, which boils at 140—141° under 13 mm. pressure. G. Y.

Oxidation of Acyloins of the Fatty Series: some α-Diketones and their Derivatives. LOUIS BOUVEAULT and RENÉ LOCQUIN (*Bull. Soc. chim*, 1906, [iii]. **35**, 650—654. Compare Abstr., 1905, i, 573, and this vol., i, 782, 783, 784).—The authors confirm Ponzio's observation (Abstr., 1901, i, 452) that acyloins are not readily converted into α-diketones by the usual oxidising agents. They find, however, that yields of 50 per cent. and upwards of the diketones can be obtained by the application of Sabatier and Senderens' catalytic process (Abstr., 1903, i, 454, and 1905, i, 254) to the acyloins. The authors now find that the statement formerly made (Locquin, Abstr., 1905, i, 20), that the higher α-diketones which do not contain the $\mathrm{CH_3{\cdot}CO}$ group do not form sodium hydrogen sulphite compounds, is inaccurate; the compounds are, however, unstable and difficult to isolate in these cases.

Diisobutyryl has a sp. gr. 0·912 at 4°/0° and boils at 144—145°. The *monoxime* boils at 135° under 10 mm. pressure, and the *dioxime* crystallises from boiling benzene and melts at 171·5°. When di*iso*butyryl is treated with magnesium methyl iodide, a *product* is obtained, which boils at 75—80° under 11 mm. pressure, and may have the constitution $\mathrm{COPr^{\beta}{\cdot}CMePr^{\beta}{\cdot}OH}$. With magnesium phenyl bromide, a liquid is produced, which boils at 137° under 11 mm. pressure and may consist of the *substance* $\mathrm{COPr^{\beta}{\cdot}CPhPr^{\beta}{\cdot}OH}$, with a trace of its dehydration product, $\mathrm{COPr^{\beta}{\cdot}CPh{:}CMe_2}$. T. A. H.

Influence of some Mineral Matters on the Liquefaction of Starch. JULES WOLFF and AUGUSTE FERNBACH (*Compt. rend.*, 1906, **143**, 363—365).—It was previously shown (*ibid.*, May 15, 1906) that the lime present in starch has considerable influence on the viscosity. Experiments with starch, previously washed until nearly free from calcium and magnesium, showed that ammonia, sodium carbonate, magnesium carbonate, and calcium carbonate have about the same effect, whilst alumina is without action.

When starch containing the usual bases is treated with sulphuric or phosphoric acid until about neutral (methyl-orange), it very readily loses its viscosity when heated under pressure. N. H. J. M.

Mechanism of the Influence of Acids, Bases, and Salts in the Liquefaction of Starch Paste. Auguste Fernbach and Jules Wolff (*Compt. rend.*, 1906, **143**, 380—383. Compare Abstr., 1904, i, 211, 374; 1905, i, 164, 574, 624; preceding abstract). When starch paste is made neutral to methyl-orange by the addition of sulphuric acid and then heated at 120°, its viscosity is very greatly diminished, but if disodium hydrogen phosphate is added to the neutralised paste before heating, the viscosity is increased, and becomes equal to that of the original paste when the quantity of the salt added is two and a half times that of the equivalent of the acid. The addition of neutral salts, such as magnesium or calcium sulphate or of sodium dihydrogen phosphate, to the neutralised starch paste effects no change in its viscosity, nor is the viscosity of the original paste changed by the addition of disodium hydrogen phosphate or of sodium dihydrogen phosphate. The effect of sodium hydroxide in retarding the liquefaction of neutralised starch paste is much more marked than that of disodium hydrogen phosphate. It follows, therefore, that the liquefaction of neutralised starch paste is partly due to the transformation of the secondary phosphates present in the starch into primary phosphates, that it is not affected by the addition of salts neutral to methyl-orange, but is retarded by the addition of salts alkaline to this reagent, and checked altogether by traces of free alkali.

M. A. W.

Starchy Substances studied by the aid of our knowledge of the Colloidal State. G. Malfitano (*Compt. rend.*, 1906, **143**, 400—403).—A theoretical paper. Fernbach has shown that starch contains 0·2 per cent. of phosphorus in the form of phosphates even after maceration with hydrochloric acid (Abstr., 1904, i, 294); the author therefore regards a clear starch solution as a colloidal solution in which the granules are formed of starch molecules grouped round the $\vdots PO_4$ ion, $[(C_6H_{10}O_5)nPO_4]\vdots$, the composition varying with the nature of the free electrolytes in the liquid medium, and subject to the laws already established in the case of a colloidal solution of ferric hydroxychloride (compare Abstr., 1905, ii, 459; this vol., ii, 33, 450, 526). M. A. W.

Action of Acyl Chlorides on Mixtures of Amines. Frank B. Dains (*J. Amer. Chem. Soc.*, 1906, **28**, 1183—1188).—This investigation was carried out with the object of ascertaining whether, when a mixture of two amines in molecular proportions is treated with an acyl chloride, any preference is shown as to the amine attacked, and also of determining the conditions which govern any such preference. The results show that when there is any appreciable difference of basicity between the two amines, the acyl derivative of the more negative is largely or exclusively produced together with the salt of the more positive amine. E. G.

Compounds of Chromium Tetroxide with Ethylenediamine and Hexamethylenetetramine. KARL A. HOFMANN (*Ber.*, 1906, **39**, 3181—3184).—*Ethylenediamine chromate*, $H_2CrO_4,C_2H_8N_2$, prepared by the addition of ethylenediamine hydrate to an aqueous solution of chromic acid, forms orange-coloured, tetragonal plates, and is sparingly soluble in water.

The *compound* $CrO_4,C_2H_8N_2,2H_2O$, prepared by cooling in ice the filtrate obtained from a mixture of chromic acid, water, and ethylenediamine hydrate and then adding hydrogen peroxide, forms a glistening, greyish-green, crystalline powder, which deflagrates on heating.

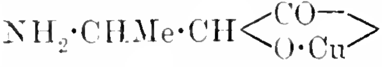
The *compound* $CrO_4,C_6H_{12}N_4$, prepared in a similar manner from hexamethylenetetramine, separates in "reddish-brownish-yellow" hexagonal crystals. When heated it deflagrates. A. McK.

Ethylene- and Propylene-diamine Compounds of Palladium. ALEXANDER GUTBIER and M. WOERNLE (*Ber.*, 1906, **39**, 2716—2720. Compare Abstr., 1905, i, 584, 876; ii, 534; this vol., i, 244, 402).—When an aqueous solution of ethylenediamine or propylenediamine is added to one of a palladous haloid, rose- or flesh-coloured precipitates are obtained, having the composition PdD_2X_2,PdX_2 (where D is the diamine and X is chlorine or bromine). They are soluble in excess of the base, and from the yellow solutions dilute halogen acids precipitate yellow needles of the palladosammines.

Palladous ethylenediamine chloride, $PdDCl_2$, *bromide*, $PdDBr_2$, *iodide*, $PdDCl_2$, and the corresponding propylenediamine compounds, dissolve in concentrated halogen acids, forming dark-coloured solutions, from which, on cooling, substances of the preceding type separate. Substances of the type $PdX_2,D,2HX$ have been prepared, and are capable of combining with two atoms of halogen to form compounds of the type $PdX_4,D,2HCl$. C. S.

Synthesis of Hydroxy- and Diamino-acids. III. αα-Diaminoazelaic Acid, αβ-Diaminobutyric Acid, and β-Amino-α-hydroxybutyric Acid. CARL NEUBERG and MAX FEDERER (*Chem. Centr.*, 1906, ii, 764—766; from *Biochem. Zeit.*, 1, 282—298. Compare Abstr., 1905, i, 687).—When treated with bromine in presence of phosphorus, azelaic acid yields αα-dibromoazelaic acid in the form of a yellow, non-crystallisable oil. When heated with concentrated ammonia and ammonium carbonate at 120—125°, this yields *αα-diaminoazelaic acid* in the form of microscopic crystals, which dissolve in hot water and are readily soluble in alkali hydroxides or mineral acids. It forms insoluble copper, silver, mercury, and lead salts, and combines with phenylcarbimide to form a crystalline phenylhydantoic acid, which melts at about 120°; the diethyl ester is an oil.

αβ-Diaminobutyric acid was obtained from αβ-dibromobutyric acid in a similar manner in 24 per cent. yield. With phenylcarbimide, it yields a crystalline compound, $C_{18}H_{20}O_4N_4$, melting at 238°. With picric acid it yields a picrate, $C_{10}H_{13}O_9N_5,2H_2O$, which is hygroscopic and decomposes at about 90°.

When the product obtained by the action of concentrated ammonia is kept for some time, it deposits rhombic crystals of *β-amino-α-hydroxybutyric acid*. Iminobutyric acid is probably formed as an intermediate product, and this then combines with water. It yields a copper salt,  $NH_2\cdot CHMe\cdot CH<\begin{matrix}CO—\\O\cdot Cu\end{matrix}>O$, and with α-naphthylcarbimide it gives the crystalline *α-naphthylhydantoic acid*, which decomposes at about 170°.

H. M. D.

A New Synthesis of Serine.

Hermann Leuchs and Walter Geiger (*Ber.*, 1906, **39**, 2644—2649).—The authors describe a third method of synthesising serine, the acid having been formerly synthesised by Erlenmeyer, jun. (Abstr., 1903, i, 29) and by E. Fischer and Leuchs (Abstr., 1903, i, 12).

When chloroacetal, $CH_2Cl\cdot CH(OEt)_2$, is heated with sodium ethoxide it forms ethoxyacetal, $OEt\cdot CH_2\cdot CH(OEt)_2$, which, when boiled with dilute sulphuric acid, is converted into ethoxyacetaldehyde, $OEt\cdot CH_2\cdot CHO$. The isolation of this product from the reaction mixture was not necessary, since the latter may be submitted directly to the cyanohydrin reaction by consecutive treatment with ammonia, hydrogen cyanide, and hydrochloric acid, when β-ethoxy-α-alanine, $OEt\cdot CH_2\cdot CH(NH_2)\cdot CO_2H$, is formed. The latter compound need not be isolated, since when the reaction mixture is boiled with concentrated hydrobromic acid the following action takes place:

$$OEt\cdot CH_2\cdot CH(NH_2)\cdot CO_2H + HBr = OH\cdot CH_2\cdot CH(NH)_2\cdot CO_2H + EtBr.$$

The yield of serine obtained in this manner is 35—40 per cent. of the theoretical, calculated on the ethoxyacetal used.

Various derivatives of β-ethoxy-α-alanine, serine, and ethoxyacetaldehyde are described.

γ-Phenyl-α-hydroxymethylhydantoin, $C_{10}H_{10}O_3N_2$, prepared by evaporating to dryness a mixture of the alkaline solution of β-hydroxy-α-phenylureidopropionic acid and hydrochloric acid, separates from water in needles and melts at 168—169° (corr.).

Ethyl carboxymethylserine, $CO_2Me\cdot NH\cdot CH(CH_2\cdot OH)\cdot CO_2Et$, was prepared as follows: a current of dry hydrogen chloride was passed through an ethyl-alcoholic solution of serine until the latter had dissolved and the mixture then heated for one hour at 100°. The free ethyl serine was then liberated from the resulting hydrochloride and treated with a mixture of methyl chlorocarbonate and sodium carbonate. Ethyl carboxymethylserine is a viscid oil, which boils at 181—182° under 12 mm. pressure.

β-Ethoxy α-alanine, $OEt\cdot CH_2\cdot CH(NH_2)\cdot CO_2H$, may be obtained as an intermediate product in the synthesis of serine just described and melts and decomposes at 256° (corr.). Its aqueous solution has a sweet taste, reacts faintly acid towards litmus, and assumes a deep blue tint when boiled with copper oxide. It is sparingly soluble in water and separates from 90 per cent. alcohol in needles. Its *copper* salt is described. When heated with concentrated hydrochloric acid, it is converted into serine.

β-Ethoxy-α-phenylureidopropionic acid,

$OEt \cdot CH_2 \cdot CH(NH \cdot CO \cdot NHPh) \cdot CO_2H$,

prepared by the addition of phenylcarbimide to a solution of the ethoxyalanine in sodium hydroxide, separates from water in hexagonal plates and melts at 167—168° (corr.).

Ethoxyacetaldehydesemicarbazone, $OEt \cdot CH_2 \cdot CH:N \cdot NH \cdot CO \cdot NH_2$, prepared by the addition of semicarbazide hydrochloride to ethoxyacetaldehyde ammonia (m. p. 79—81°), separates from water in rhombohedra and melts at 85—86°. A. McK.

Resolution of Racemic Serine into the Optically Active Components. Emil Fischer and Walter A. Jacobs (*Ber.*, 1906, **39**, 2942—2950).—p-*Nitrobenzoyl*-dl-*serine*, prepared by the gradual addition of *p*-nitrobenzoyl chloride and potassium hydroxide to serine in the cold, crystallises from water in light yellow, thin needles, which sinter at 184° (corr.) and melt and decompose to a brown liquid at 206—207° (corr.). After heating with quinine in alcohol, the quinine salt of the *d*-compound separates on cooling and on hydrolysis yields p-*nitrobenzoyl*-d-*serine*, crystallising in glistening, faintly yellow plates which sinter at 171° (corr.) and melt at 189·5° (corr.). It has $[\alpha]_D - 43·74°$ at 20°. d-*Serine*, obtained from the foregoing on heating with hydrogen bromide, crystallises in large, colourless prisms or hexagonal plates which, on heating, become brown at 211° (corr.) and decompose about 228° (corr.). It has $[\alpha]_D + 6·87°$ at 20° in water and $-14·32°$ in *N*-hydrochloric acid and is approximately twice as soluble in water as racemic serine. The quinine salt of the *l*-compound is obtained from the mother liquors: to purify it, it is converted into the *brucine* salt, which crystallises in yellow prisms aggregated in rays. p-*Nitrobenzoyl*-l-*serine* is in every way similar to the *d*-compound, but has $[\alpha]_D + 43·56°$ at 20°. Similarly, *l*-serine has $[\alpha]_D - 6·83°$ at 20° in water and $+14·45°$ in *N*-hydrochloric acid. *d*-Serine has a definitely sweet taste; that of *l*-serine is less, although still appreciably sweet. l-*Serine methyl* ester was obtained as a colourless, strongly alkaline syrup; the *hydrochloride* consists of colourless four- or eight-sided microscopic plates decomposing at 167° (corr.). l-*Serine anhydride* forms slender, colourless needles melting and decomposing at 247° (corr.); it has $[\alpha]_D - 67·46°$ at 20°, and is identical with a product derived from silk fibroin. *l*-Serine is therefore regarded as the natural product.

The authors have also resolved *iso*serine and diaminopropionic acid. *Benzoyl*iso*serine* has $[\alpha]_D + 10·45°$ at 20°, whilst the isomeric *dibenzoyldiaminopropionic acids* show $[\alpha]_D - 35·76°$ and $+35·9°$ at 20° respectively. E. F. A.

Behaviour of Racemic Amino-acids towards Yeast. New Biological Method for resolving them. Felix Ehrlich (*Zeit. Ver. deut. Zuckerind.*, 1906, **608**, 840—860).—Racemic amino-acids are readily attacked by yeast in solutions containing a large proportion of sucrose. The yeast should be poor in nitrogen and should be used in large excess, in order that the destruction of one of the component amino-acids may be complete. Any ordinary clean baker's yeast is suitable, pure cultures of the pressed yeasts of Classes II and XII giving especially good results. These yeasts can now be procured very constant in composition, the dry matter they contain amounting to about 25 and the nitrogen to about 2 per cent.

Ten grams of the racemic amino-acid and from 200 to 300 grams of sucrose are dissolved in 2 to 3 litres of water contained in a capacious flask, and the solution, which need not be sterilised, mixed with a quantity of pressed yeast varying, for different amino-acids, from 50 to 150 grams. The flask is closed by means of a sulphuric acid seal and is vigorously shaken for some time. The fermentation is allowed to proceed at the ordinary temperature, since, if higher temperatures are employed, the autolytic activity of the yeast becomes greater, and an increased amount of the yeast-substance is thus introduced into the solution. When the liquid no longer reduces Fehling's solution or gives the naphthol reaction, the fermentation is complete; this is generally found to be the case after thirty-six to forty-eight hours, whilst in some cases twenty-four hours are sufficient. The clear liquid is syphoned off and the residual yeast placed on a large filter and washed with a little water. The whole of the solution is then mixed with a little alumina cream or kieselguhr and filtered, the clear liquid thus obtained giving no biuret reaction and only a faint Millon's reaction. The solution is boiled to a volume of 100—200 c.c., filtered, if necessary, after the addition of animal charcoal, and evaporated on the water-bath to a thin syrup. While the latter is cooling, crystallisation is started by scratching the dish with a glass rod.

If the specific rotation of the product indicates the presence of racemic compound, a second fermentation should be carried out in the same way as the first.

From the compounds examined by the author, namely, racemic alanine, leucine, and *a*-amino*iso*valeric acid, *l*-alanine, *d*-leucine, and *l*-*a*-amino*iso*valeric acid were obtained in a pure state in yields amounting respectively to 65, 76, and 67 per cent. of the theoretical quantities. In all cases both optical isomerides are attacked by the yeast, but, as a rule, one far more rapidly than the other.

In hydrochloric acid solution, *d*-leucine has $[\alpha]_D$ $-15 \cdot 4°$ at 20° (compare Fischer and Warburg, this vol., i, 72).

When submitted to the action of yeast in the manner described, synthetical *a*-amino-*a*-methylbutyric acid yields a lævorotatory compound, and, with a mixture of *d*-*iso*leucine and *d*-allo*iso*leucine, obtained either synthetically from *d*-amyl alcohol or by the action of barium hydroxide solution on natural *d*-*iso*leucine, the latter gives up its nitrogen to the yeast and is converted into *d*-amyl alcohol, whilst the *d*-allo*iso*leucine is not appreciably attacked. T. H. P.

Synthesis of Polypeptides. XV. Emil Fischer (*Ber.*, 1906, 39, 2893—2931).—*a-Bromo*iso*hexoyltetraglycylglycyl chloride* is prepared from bromo*iso*hexoyltetraglycylglycine by the action of acetyl chloride and phosphorus pentachloride in the apparatus previously described (Abstr., 1905, i, 863). The glycine must be specially prepared for chlorination by solution in cold alkali hydroxide and slow precipitation with hydrochloric acid and subsequent drying in a vacuum;

if crystallised from water or alcohol, the carboxyl group of the polypeptide resists all attempts at chlorination.

*α-Bromo*iso*hexoyl-pentaglycylglycyl chloride* and *-hexaglycylglycyl chloride* are obtained as colourless solids in a similar manner.

*α-Bromo*iso*hexoylhexaglycylglycine*,

$$C_4H_9\cdot CHBr\cdot CO\cdot[NH\cdot CH_2\cdot CO]_6\cdot NH\cdot CH_2\cdot CO_2H,$$

is prepared by condensation of triglycylglycine with α-bromo*iso*hexoyl-diglycylglycine chloride in presence of sodium hydroxide, special experimental precautions being necessary to ensure success; it is obtained as a loose, colourless powder which, when quickly heated, turns yellow at about 245° (corr.) and melts and decomposes between 256° and 259° (corr.).

Leucylhexaglycylglycine,

$$C_4H_9\cdot CH(NH_2)\cdot CO\cdot[NH\cdot CH_2\cdot CO]_6\cdot NH\cdot CH_2\cdot CO_2H,$$

obtained by the action of liquid ammonia on the foregoing, is obtained as a microcrystalline, colourless powder with H_2O which, when rapidly heated, becomes yellow at about 200° and darkens and finally decomposes between 280° and 290°. It dissolves in hot hydrochloric acid, forming a sparingly soluble *hydrochloride*, and shows a marked biuret coloration.

*α-Bromo*iso*hexoyloctaglycylglycine* is prepared by coupling pentaglycylglycine with α-bromo*iso*hexoyldiglycylglycyl chloride in presence of alkali; it turns yellow between 244° and 255° (corr.) and finally decomposes at about 288° (corr.). *Leucyloctaglycylglycine*,

$$C_4H_9\cdot CH(NH_2)\cdot CO\cdot[NH\cdot CH_2\cdot CO]_8\cdot NH\cdot CH_2\cdot CO_2H,$$

crystallises with H_2O, the dry substance being hygroscopic; it colours at 255° (corr.) and becomes black at 290° (corr.). *α-Bromo*iso*hexoyl-decaglycylglycine* turns yellow at 230°, becomes brown above this, and black at about 293° (corr.); the alkaline solution gives a biuret coloration. *Leucyldecaglycylglycine*,

$$C_4H_9\cdot CH(NH_2)\cdot CO\cdot[NH\cdot CH_2\cdot CO]_{10}\cdot NH\cdot CH_2\cdot CO_2H,$$

is a colourless, amorphous powder without a melting point; it shows a strong biuret coloration, is easily soluble in cold fuming hydrochloric acid, the *hydrochloride* being precipitated on dilution; the solution in dilute ammonia gives a dense precipitate with ammonium sulphate, and in this respect strongly resembles the natural proteids.

Active *α-bromo*iso*hexoyldiglycylglycine*, prepared by condensation of diglycylglycine with α-bromo*iso*hexoyl chloride from *d*-leucine, sinters at 163° (corr.) and melts at 168—169° (corr.) to a yellow liquid. In normal alkali it has $[\alpha]_D$ +31·98° at 20°. l-*Leucyldiglycylglycine*, $C_4H_9\cdot CH(NH_2)\cdot CO\cdot[NH\cdot CH_2\cdot CO]_2\cdot NH\cdot CH_2\cdot CO_2H$, prepared by the action of aqueous ammonia on the preceding compound, forms stellar aggregates of glistening, prismatic crystals which, when quickly heated, become yellow at 220° (corr.) and melt at 230—232° (corr.), partially decomposing to a reddish-brown liquid. It has in aqueous solution $[\alpha]_D$ +45·85° at 20° and gives a marked biuret coloration.

d-*α-Bromo*iso*hexoylglycine*, prepared from *d*-α-bromo*iso*hexoic acid and glycine, softens at 82° and melts at 85—86° (corr.). It crystallises in stellar aggregates of long needles from alcohol, in which solvent it has $[\alpha]_D$ +62·0° at 20°. l-*Leucylglycine*,

$$C_4H_9\cdot CH(NH_2)\cdot CO\cdot NH\cdot CH_2\cdot CO_2H,$$

sinters at 235° and melts at 248° (corr.), being partially converted into anhydride; it crystallises in needles and is more soluble in water than the racemic form; it tastes somewhat bitter, forms a deep blue copper salt, and has $[\alpha]_D$ +85·5° at 20°.

l-*Leucylglycine anhydride*,  $C_4H_9·CH<\begin{matrix}NH·CO\\CO·NH\end{matrix}>CH_2$, prepared under special precautions from the ester of the dipeptide, sinters at 245° and melts at 254—255° (corr.); it tastes bitter, reacts neutral, and shows $[\alpha]_D$ +32·3° at 20°. This anhydride is identical with a product obtained by Fischer and Abderhalden by the hydrolysis of elastin (this vol., i, 719).

d-α-*Bromo*iso*hexoyl*-d-*alanine* crystallises in thin, long needles which soften at 96° and melt at 101—103° (corr.) and have $[\alpha]_D$ +23·0° at 20°.

l-*Leucyl* d-*alanine*, $C_4H_9·CH(NH_2)·CO·NH·CHMe·CO_2H$, forms flat, right-angled plates which taste bitter and melt at 257° (corr.); the *copper* salt crystallises in flat, blue prisms. The dipeptide dissolved in methyl alcohol gives $[\alpha]_D$ +23·7° at 20°. α-*Leucyl*-d-*alanine anhydride*,  $C_4H_9·CH<\begin{matrix}NH·CO\\CO·NH\end{matrix}>CHMe$, crystallises in long needles melting at 258° (corr.), tastes bitter, and has $[\alpha]_D$ −29·0° at 20°.

d-α-*Bromo*iso*hexoyl*-l-*leucine* crystallises in microscopic, double pyramids, melting at 149° (corr.), and has $[\alpha]_D$ +16·2° at 20°. l-*Leucyl*-l-*leucine*, $C_4H_9·CH(NH_2)·CO·NH·CH(C_4H_9)·CO_2H$, crystallises from water or alcohol in long, pointed plates aggregated in rosettes which melt at 270° (corr.) and have $[\alpha]_D$ − 13·43° at 20° in alkaline solution. It forms a crystalline *hydrochloride* and a blue *copper* salt separating in needles, and a characteristic *carbethoxy*-l-*leucyl*-l-*leucine*, of which the obliquely-cut plates melt at 149—150° (corr.) and are sparingly soluble even in hot water. l-*Leucine anhydride* (*l*-leucineimide), prepared from the methyl ester of the dipeptide, melts at 277° (corr.) and has $[\alpha]_D$ − 42·8° at 20°.

l-*Bromopropionylglycylglycine* crystallises in colourless prisms melting at 172° (corr.). l-*Alanylglycylglycine*,

$$NH_2·CHMe·[CO·NH·CH_2]_2·CO_2H,$$

forms colourless, centimetre long needles, belonging to the monoclinic, hemimorphous system, with H_2O, which become yellow at 205° and melt and decompose at 245° (corr.). It does not show a biuret coloration, and gives a precipitate with phosphotungstic acid. The aqueous solution has $[\alpha]_D$ − 29·2° at 20°. The *methyl* ester crystallises in colourless, glistening plates; it liquefies between 90° and 95°, and forms a *hydrochloride*, crystallising in bundles of needles, which melts at 178° (corr.). On heating at 100°, it is converted into the *ester* of the hexapeptide, a compound sintering at 175° and melting and decomposing at 185°, which gives a marked biuret coloration, and is hydrolysed by sodium hydroxide to l-*alanyldiglycyl*-l-*alanylglycylglycine*. This decomposes at 207° and has $[\alpha]_D$ +13° at 21°.

Triglycylglycine methyl ester, prepared by esterifying the tetrapeptide with methyl alcohol and hydrogen chloride, crystallises in microscopic, glistening needles or thin sheaves of prisms: it becomes yellow at 200° and decomposes at 240°. The *hydrochloride* forms microscopic platelets which melt at 198—200°. It gives a brilliant biuret coloration, and does not condense on heating to 100°.

Methods are described for preparing formyl -*d*-, -*l*-, and -*dl*-leucine, and the measurements of their rhombic crystals given. Better methods of preparing *d*-*a*-bromo*iso*hexoic acid, *d*-*a*-bromo*iso*hexoyl chloride, and glycine anhydride are also described. E. F. A.

Dithiocarbamoglycollic Acid (Carboxymethyldithiourethane). B. Holmberg (*Ber.*, 1906, **39**, 3068—3069. Compare Abstr., 1905, i, 323).—*Dithiocarbamoglycollic acid* (*carboxymethyldithiourethane*), $NH_2{\cdot}CS{\cdot}S{\cdot}CH_2{\cdot}CO_2H$, is obtained when sulphuric acid is added to an aqueous solution of sodium chloroacetate and ammonium dithiocarbamate; it crystallises in needles or leaflets, darkens at 100°, and melts at 136—137°, yielding after a few minutes at the latter temperature the *anhydride*,

$S\Big<\begin{array}{l}CS{-}NH\\ \quad\;\;\vert\\ CH_2{\cdot}CO\end{array}$

, which crystallises in large, yellow leaflets, melts and decomposes at 168—169°, and is also obtained by acidifying the mixture of sodium chloroacetate and ammonium dithiocarbamate with acetic acid, or in accordance with the equation $CH_2SH{\cdot}CO_2H + CS(NH_2)_2 = C_3H_3ONS_2 + NH_3 + H_2O$. C. S.

A New Group of Nitrogenous Carbohydrates. Th. R. Offer (*Beitr. chem. Physiol. Path.*, 1906, **8**, 399—405. Compare Fränkel, Abstr., 1899, i, 396; Fränkel and Kelly, *ibid.*, 1902, i, 479).—A nitrogenous carbohydrate, which gives the pentose reactions, but reduces Fehling's solution after hydrolysis, has been isolated from horse's liver by extraction with alcohol after other substances had been removed by repeated extraction with acetone. Better yields are obtained by extracting the liver with hot water. After concentration of the clear extract, removal of proteids and glycogen, and further concentration and addition of methyl alcohol, a precipitate was obtained, which, after purification, was converted into its *copper* derivative, $C_{10}H_{16}O_7N_2(CuO)_2$. The corresponding carbohydrate is probably a dipentosamine, $2(C_5H_7O_3{\cdot}NH_2) + H_2O$.

From the alcoholic filtrate, a *barium* compound, $C_{14}H_{22}O_9N_2Ba$, has been obtained; this corresponds with a *diacetylated* dipentosamine, $C_{10}H_{18}O_7N_2Ac_2$. The barium compound is readily soluble in water or alcohol, but insoluble in ether or methyl alcohol. It does not reduce Fehling's solution until boiled with hydrochloric acid, and gives the characteristic pentose reactions only after prolonged boiling. J. J. S.

Chloro-derivatives of Diacetamide. Hermann Finger (*J. pr. Chem.*, 1906, [ii], **74**, 153).—*Hexachlorodiacetamide*, $NH(CO{\cdot}CCl_3)_2$, prepared by heating trichloroacetonitrile with trichloroacetic acid in a sealed tube at 180—190°, crystallises from light petroleum, melts at 81°, and is decomposed by alcohol, forming ethyl trichloroacetate and trichloroacetamide, or by ammonia, forming 2 mols. of trichloroacetamide, or by prolonged heating at 120—140°, yielding trichloroacetonitrile, trichloroacetamide, and hexachloroacetic anhydride. G. Y.

Action of Sodium Hypobromite on some Amino-compounds. J. Stuhetz (*Monatsh.*, 1906, 27, 601—605).—The action of sodium hypobromite on carbamide in aqueous solutions of different concentrations at the ordinary temperature and pressure leads to the evolution of 29·3—44·4 per cent. of nitrogen; the theoretical percentage, 46·6, was not evolved in any experiment.

Glycine, alanine, leucine, glutamic acid, tyrosine, lysine, and histidine yield only very small quantities of nitrogen when treated with sodium hypobromite solution, whilst under the same conditions arginine evolves about 1/3 of its nitrogen. G. Y.

Salts of Cuprothiocarbamides. Volkmar Kohlschütter and C. Brittlebank (*Annalen*, 1906, 349, 232—268. Compare Rathke, Abstr., 1884, 1017; Rosenheim and Loewenstamm, Abstr., 1903, i, 325; Kohlschütter, *ibid.*, 468).—The greater part of this work has been published previously. The authors agree with Rosenheim and Stadler (this vol., i, 407) that the complex salts formed by thiocarbamide with cuprous chloride have the formulæ $Cu(CH_4N_2S)Cl_2$, $Cu(C_6H_4N_2S)_2Cl$, and $Cu(CH_4N_2S)_3Cl$, the last on hydrolysis yielding the salt $[Cu(CH_4N_2S)_2H_2O]Cl$.

The complex compound, $Cu(CH_4N_2S)_3Cl$, is to be regarded as a salt of the univalent cation, $[Cu(CH_4N_2S)_3]^+$, as on electrolysis with a current density of 0·02 ampere, the cathode vessel contains finally copper and thiocarbamide in the proportion 1 : 3·01; the abnormal conductivity results obtained with this salt are discussed and found to be in agreement with Kohlschütter's conclusions (*loc. cit.*). Contrary to Kohlschütter's statement, the oxalate formed on addition of oxalic acid to the chloride has the formula $Cu(CH_4N_2S)_3C_2HO_4,H_2O$, whilst that formed by addition of potassium oxalate has the formula

$$Cu(CH_4N_2S)_3C_2O_4.$$

The *salt* $Cu(CH_4N_2S)_3NO_3,4[Cu(CH_4N_2S)_2H_2O]NO_3$ crystallises in slender needles when dilute nitric acid is added to a saturated solution of the salt $Cu(CH_4N_2S)_3NO_3,[Cu(CH_4N_2S)_2H_2O]NO_3$. The comparison of the degree of electrolytic dissociation of the salt

$$[Cu(CH_4N_2S)_2H_2O]NO_3,$$

$a = 0·39$ with $v = 51·3$, with the molecular conductivity, $a = 0·86$ with $v = 32$, shows that the part of the salt which is not electrolytically dissociated consists of polymeric molecules, and the solid salt is an association of several molecules of the above formula. The *sulphate*, $[Cu(CH_4N_2S)_3][Cu(CH_4N_2S)_2H_2O]SO_4,H_2O$, *hydrogen sulphate*,

$$[Cu(CH_4N_2S)_2H_2O]HSO_4,$$

oxalate, $[Cu(CH_4N_2S)_2H_2O]_2C_2O_4$, and *perchlorate*,

$$Cu(CH_4N_2S)_3Cl,2[Cu(CH_4N_2S)_2H_2O]ClO_4,$$

are described.

The solubility of thiocarbamide in water increases on addition of cuprothiocarbamide chloride in proportion to the amount of the chloride added; similarly, the solubility of the chloride in water is increased by the presence of thiocarbamide, showing that a further addition of thiocarbamide to the cuprotrithiocarbamide takes place, which is in agreement with the results of the cryoscopic mol. weight determination.

Cuprodithiocarbamide chloride, $Cu(CH_4N_2S)_2Cl$, formed by the action of potassium chloride on cuproaquodithiocarbamide nitrate, is a salt of the type of triaminecobalt nitrite, and is only very slightly dissociated.

The bearing of the behaviour of cuprodithiocarbamide chloride on the theory of the influence of the anion on the formation of complex cations is discussed.

Cuprothiocarbamide chloride, $Cu(CH_4N_2S)Cl$, which occurs in two modifications, resembles cuprous chloride in its behaviour, dissolving in concentrated hydrochloric acid and, although less readily, in saturated sodium chloride solution; the solution in hydrochloric acid absorbs carbon monoxide. On electrolysis of the cupro-chloride in hydrochloric acid solution, the amount of thiocarbamide at the cathode diminishes in consequence of the wandering of anions containing thiocarbamide. G. Y.

***iso*Butylhydantoic Acid and Detection of Small Quantities of Leucine.** FRITZ LIPPICH (*Ber.*, 1906, **39**, 2953—2956).—Baumann and Hoppe-Seyler formerly observed that hydantoic acid was produced when a solution of glycine and carbamide was boiled with baryta water until the evolution of ammonia ceased. Similarly, Pinner and Spilker (Abstr., 1889, 704) prepared *iso*butylhydantoin from *iso*valeraldehyde hydrocyanide and carbamide, and thence obtained the *iso*butylhydantoic acid corresponding with leucine by boiling with baryta water. It is probable that the reaction (the formation of hydantoic acids) is general for all the α-aminocarboxylic acids, and a preliminary experiment with aminovaleric acid has confirmed this supposition. The reaction may be used to detect small quantities of leucine in a mixture of other amino-acids. For example, a mixture of 1 gram of leucine, 0·5 gram of glycine, and 0·5 gram of tyrosine was boiled with carbamide and baryta water in moderate excess until the evolution of ammonia had ceased, the excess of barium was removed by carbon dioxide, and the filtrate cautiously acidified with acetic acid. The crystalline precipitate thus obtained was recrystallised from 50 per cent. alcohol, when the substance separated in aggregates of well-defined, colourless needles melting at 205°. The properties of this substance show that it is identical with Pinner and Spilker's *iso*butylhydantoic acid. On account of the sparing solubility of the free *iso*butylhydantoic acid and the great solubility of its crystallisable barium salt, this reaction may be generally applied to the detection of leucine, and as little as 0·01 gram of the pure amino-acid may be distinguished in this way. G. T. M.

Specific Rotation of Glutamine. ERNST SCHULZE (*Ber.*, 1906, **39**, 2932—2933. Compare Abstr., 1885, 759).—Seven preparations of glutamine from various vegetable sources were found to have $[\alpha]_D$ between $+1·9°$ and $+9·5°$, the differences being probably due to the preparations containing the two stereoisomerides in varying proportions. E. F. A.

Complex Compounds of Organic Imides. Succinimide Nickel Derivatives. LEO TSCHUGAEFF (*Ber.*, 1906, **39**, 3190—3201. Compare Abstr., 1904, i, 478; 1905, i, 865).—The succinimide nickel group, $(Su)_2Ni$ [$Su = C_2H_4(CO)_2N$], combines with aliphatic monoamines to form a series of compounds, $(Su)_2Ni,2a$ [a = an amine], which resemble in general character the copper compounds already described. The compounds in question are prepared according to two methods: (1) Interaction of nickel salts and amines in presence of a slight excess of succinimide, the action, which is conducted in alcoholic solution, being in accordance with the scheme $NiX_2 + 2SuH + 4a = Ni(Su)_2,2a + 2a,HCl$. (2) Action of amines on nickel succinimide octahydrate, the reaction taking place either at the ordinary temperature or on gentle warming in the presence of a little alcohol, thus: $(Su)_2Ni,8H_2O + 2a = (Su)_2Ni,2a + 8H_2O$.

The compounds $(Su)_2Ni,2a$ form yellow needles, and undergo no change when kept under diminished pressure over sulphuric acid. They are also moderately stable towards heat, and begin to decompose above 200°. Solutions in water and in alcohol are bluish-green and unstable. Aqueous solutions readily undergo hydrolytic dissociation, with separation of nickelous hydroxide. The compounds are readily decomposed by acids, thus: $(Su)_2Ni,2a + 4HX = 2SuH + 2aHX + NiX_2$. The following compounds are described: *methylamine* compound, $(Su)_2Ni,2Me\cdot NH_2$; *propylamine* compound, $(Su)_2Ni,2Pr\cdot NH_2$; iso*butylamine* compound, $(Su)_2Ni,2C_4H_9\cdot NH_2$; *allylamine* compound, $(Su)_2Ni,2C_3H_5\cdot NH_2$; *camphylamine* compound,

$$(Su)_2Ni,2C_{10}H_{17}\cdot NH_2,2H_2O;$$

the latter forms lilac needles.

The only compound obtained from a secondary amine was a yellow, crystalline, very unstable compound from dimethylamine and the octahydrate, whilst tertiary amines do not form double compounds with succinimide.

When an excess of succinimide is added to a concentrated solution of nickel chloride or of nickel acetate, and trimethylamine is then added to the warm solution, the *octahydrate*, $(Su)_2Ni,8H_2O$, separates as bright blue needles.

Triethylenediamine nickel succinimide, $C_{14}H_{32}O_4N_8Ni,2H_2O$, prepared by the action of ethylenediamine on the octahydrate, crystallises in reddish-violet prisms. It decomposes at about 200°. Its aqueous solutions are reddish-violet.

Propylenediamine and butylenediamine also react with the octahydrate. The *compound* $C_8H_{20}N_6S_2Ni$ is formed when potassium thiocyanate is added to the solution obtained by the addition of trimethylenediamine to the octahydrate; it crystallises in lilac needles or prisms.

The action of tetramethylenediamine and pentamethylenediamine respectively on the octahydrate was also studied, but well-defined compounds were not obtained. A. McK.

Cobalt Dioximines. LEO TSCHUGAEFF (*Ber.*, 1906, **39**, 2692—2702. Compare Abstr., 1904, i, 478; 1905, i, 743, 865).—The ammine derivatives of the dioximines can be formulated in accordance with Werner's theory, the complex D_2H_2 $\left(\text{where } D = \begin{matrix} R\cdot C\colon NO\cdot \\ | \\ R\cdot C\colon NO\cdot \end{matrix}\right)$ occupying four positions in the metallic complex. Moreover, the ammonia can be replaced by methylamine, ethylamine, or pyridine.

Diamminedimethylglyoximinecobalt chloride,

$[Co(NH_3)_2D_2H_2]Cl,5H_2O$,

is obtained (1) by heating dimethylglyoxime, chloropentamminecobalt chloride (purpureochloride), and a solution of ammonium acetate on the water-bath; (2) in a similar manner from hexamminecobalt chloride (luteochloride), dimethylglyoxime, and excess of ammonium acetate; (3) from carbonatotetramminecobalt sulphate as in (2), excess of potassium or ammonium chloride being added to precipitate the chloride; (4) by passing air through a concentrated solution of cobaltous chloride, dimethylglyoxime, and excess of 10 per cent. ammonium hydroxide, ammonium chloride being finally added after the solution has been evaporated to a small bulk.

Chloroamminedimethylglyoximinecobalt, $[CoCl(NH_3)D_2H_2]$, is obtained when the first-mentioned method of preparation is carried out in the presence of acetic acid; it crystallises in dark brown needles or prisms, is stable to acids or alkalis, does not contain ionisable chlorine, and consequently does not possess electrical conductivity. Concentrated sulphuric acid dissolves the substance, forming a rose-red solution, which evolves hydrogen chloride only when heated strongly. The substance is converted into the preceding chloride by treatment with ammonium hydroxide.

Nitritoamminedimethylglyoximinecobalt, $[Co(NO_2)(NH_3)D_2H_2]$, obtained from xantho- or *iso*xantho-cobalt chloride, separates from hot water in small, yellowish-brown prisms. The nitrite group is not ionisable.

Diethylaminedimethylglyoximinecobalt chloride, $[Co(NH_2Et)_2D_2H_2]Cl$, results when air is passed for four to five hours through a solution of cobalt chloride, dimethylglyoxime, and ethylamine. It separates from hot water in small, brownish-yellow prisms or plates, and is very soluble in water. Potassium iodide or nitrate or sodium chlorate precipitate the corresponding sparingly soluble salts. The *iodide* separates from 30—40 per cent. alcohol in golden-yellow needles; the *nitrate* crystallises from hot water. The *base*, $[Co(NH_2Et)_2D_2H_2]\cdot OH$, obtained from the chloride and silver oxide, is only stable in solution; it has an alkaline reaction, absorbs carbon dioxide from the atmosphere, precipitates the hydroxides of the heavy metals, and with acids yields the corresponding salts. The solution has a yellowish-brown colour and does not smell of ethylamine.

Dipyridinedimethylglyoximinecobalt chloride, $[Co(C_5NH_5)_2D_2H_2]Cl$, obtained in 50 per cent. alcoholic solution in a similar manner to the ethylamine compound, separates in large, dark brown crystals. When it is dissolved in warm water and treated with a slight excess of potassium hydroxide, the *anhydro-base*, $[Co(C_5NH_5)_2D_2H]$, is obtained quantitatively as a dark brown, crystalline precipitate. The *nitrate*, $[Co(C_5NH_5)_2D_2H_2]NO_3$, obtained by dissolving the anhydro-base in dilute nitric acid, forms brown, nacreous leaflets, is electrolytically dissociated in aqueous solution, and yields, with potassium iodide or thiocyanate, precipitates of the corresponding salts. C. S.

Thiocyanoamminechromium Salts. VI. Chromium Salts. Alfred Werner and J. von Halban (*Ber.*, 1906, **39**, 2668—2673. Compare this vol., ii, 452).—*Thiocyanopentamminechromium thiocyanate*, $[Cr(CNS)(NH_3)_5]\cdot CNS$, is obtained when chloropentamminechromium chloride (compare Christensen, Abstr., 1893, ii, 469) is boiled with an excess of a concentrated acetic acid solution of potassium thiocyanate; it separates in aggregates of orange or reddish-brown leaflets, is easily soluble in hot water, has not been obtained pure, and yields the following salts by precipitation. The *nitrate*,

$$[Cr(CNS)(NH_3)_5]NO_3,$$

separates from dilute acetic acid in orange-yellow crystals; the *dichromate*, $[Cr(CNS)(NH_3)_5]Cr_2O_7$, crystallises in bronze-coloured needles; the *chloride*, $[Cr(CNS)(NH_3)_5]Cl_2$, is very stable to concentrated hydrochloric acid; the *bromide*, $[Cr(CNS)(NH_3)_5]Br_2$, crystallises in deep orange crystals.

Nitratopentamminechromium nitrate, $[Cr(NO_3)(NH_3)_5](NO_3)_2$, is obtained from concentrated nitric acid, and the preceding nitrate or the aquopentamminechromium base derived from the chloropentamminechromium chloride; it is sparingly soluble in cold water, and at 30—40° the colour of the solution changes from red to violet, and the nitrato-salt cannot be recovered. The *iodide*, $[Cr(NO_3)(NH_3)_5]I_2$, is obtained from the nitrate and potassium iodide.

When thiocyanopentamminechromium thiocyanate is heated at 130—140°, until the evolution of ammonia ceases, a mixture is obtained from which *dithiocyanotetramminechromium chloride*,

$$[Cr(CNS)_2(NH_3)_4]Cl,$$

and *trithiocyanotriamminechromium*, $Cr(CNS)_3(NH_3)_3$, have been isolated. The latter is insoluble in cold water, alcohol, ether, or chloroform, but dissolves in piperidine, quinoline, benzylamine, acetonitrile, or acetone, being reprecipitated by the addition of ether. C. S.

Insoluble Chromicyanides. Frederick Van Dyke Cruser and Edmund H. Miller (*J. Amer. Chem. Soc.*, 1906, **28**, 1132—1151).—Potassium chromicyanide, $K_3Cr(CN)_6$, was prepared by a modification of Christensen's method (Abstr., 1885, 737). The following salts were obtained as insoluble precipitates by adding solution of potassium chromicyanide to solutions of metallic salts.

Cadmium chromicyanide, $Cd_3Cr_2(CN)_{12}$, forms a white precipitate with a slightly green tinge. Cobalt chromicyanide, $Co_3Cr_2(CN)_{12}$, is obtained as a light rose-coloured precipitate which becomes yellowish-brown on drying. *Cuprous chromicyanide*, $Cu_3Cr(CN)_6$, forms an orange-yellow precipitate. *Cupric chromicyanide*, $Cu_3Cr_2(CN)_{12}$, is blue when first precipitated, but gradually becomes green, and when dry is reddish-purple. *Ferrous chromicyanide*, $Fe_3Cr_2(CN)_{12}$, is obtained as a brick-red, granular precipitate, which, on drying, becomes dark green. *Manganous chromicyanide*, $Mn_3Cr_2(CN)_{12}$, forms a greenish-white, crystalline precipitate, and when dry is of a light brown colour. *Nickel chromicyanide*, $Ni_3Cr_2(CN)_{12}$, forms a light greenish-blue precipitate which becomes black on drying. *Silver* *chromicyanide*, $Ag_3Cr(CN)_6$, is obtained as an orange yellow precipitate, and when dry is rose-red in colour. *Zinc chromicyanide*, $Zn_3Cr_2(CN)_{12}$, forms a yellowish-white, crystalline precipitate which becomes straw-coloured on drying.

On adding potassium chromicyanide solution to mercurous nitrate solution, a yellowish-white precipitate is produced, which rapidly darkens and finally becomes grey. It is probable that the original precipitate consists of mercurous chromicyanide, which decomposes with formation of mercurous cyanide, the latter becoming converted into mercuric cyanide and mercury.

The action of various reagents, such as the mineral acids, alkali hydroxides, and sodium peroxide, on these insoluble chromicyanides is described.

Solutions of lead acetate and nitrate of *N*/10 strength do not yield precipitates with *N*/10 potassium chromicyanide. A list is given of a large number of other salts which also fail to give a precipitate with this reagent. E. G.

Reactions at Low Temperatures. I. Cyanides. WALTER PETERS (*Ber.*, 1906, **39**, 2782—2784).—The compounds described were prepared by dissolving separately the base and hydrogen cyanide in absolute ether, cooling to −70°, and then mixing.

Diethylammonium cyanide is colourless, soluble in alcohol, and decomposes between −20° and −30°. *Triethylammonium cyanide* crystallises in needles and decomposes between −40° and −50°. *Dimethylhydrazinium cyanide* also crystallises in needles, decomposing between −6° and −10°. *Pentamethylenediaminium cyanide* soon becomes sticky, and decomposes from −40° to −50°. *Piperidinium cyanide* decomposes from −25° to −35°, whilst *coniinium cyanide* decomposes at about −40° to −50°. E. F. A.

***s*-Dimethylhydrazine.** LUDWIG KNORR and A. KÖHLER (*Ber.*, 1906, **39**, 3257—3265).—When 1-methylpyrazole methiodide (obtained quantitatively from pyrazole, methyl alcohol and methyl iodide) is heated with a concentrated solution of potassium hydroxide, formic acid and a basic oil are produced; the latter has not been thoroughly examined, but from it *s*-dimethylhydrazine has been isolated. It boils at 81° under 747 mm. pressure, has a sp. gr. 0·8274 and n_D 1·4209 at 20° (compare Harries and Klamt, Abstr., 1895, i, 262). The *acid hydrochloride*, *acid sulphate*, and *acid oxalate*, and the *picrate* and *picrolonate*, are described.

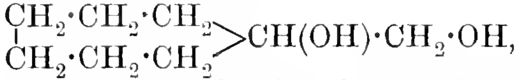
Dimethylsemicarbazide, $NH_2\cdot CO\cdot NMe\cdot NHMe$, obtained from *s*-dimethylhydrazine, hydrochloric acid, and potassium cyanate, melts at 116°. s-*Dicarbanilyldimethylhydrazine*, $N_2Me_2(CO\cdot NHPh)_2$, obtained from phenylcarbimide and the base in ethereal solution, melts and decomposes at 288°. *Phenyldimethylthiosemicarbazide*,

$$NHPh\cdot CS\cdot NMe\cdot NHMe,$$

melts at 115°. s-*Dibenzoyldimethylhydrazine*, $NMeBz\cdot NMeBz$, obtained by the Schotten-Baumann method, melts at 85°. *Dimethylpicrazide*, $C_6H_2(NO_2)_3\cdot NMe\cdot NHMe$, obtained from *s*-dimethylhydrazine and picryl chloride in alcoholic solution, melts at 141°. C. S.

Explanation of the Substitution of Aromatic Compounds. ARNOLD F. HOLLEMAN (*J. pr. Chem.*, 1906, [ii], **74**, 157—160. Compare Abstr., 1903, i, 623).—An amplification of the author's criticisms of Flürscheim's theory of substitution in the aromatic series (Abstr., 1903, i, 79; 1905, i, 614; this vol., ii, 529). G. Y.

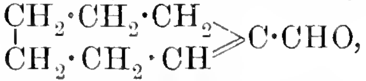
The Simplest Methylene Hydrocarbons of Various Ring Systems and their Conversion into Alicyclic Aldehydes. OTTO WALLACH [with H. KÖHLER] (*Chem. Centr.*, 1906, ii, 602; from *Nachr. k. Ges. Wiss. Göttingen*, 1906, 74—80. Compare this vol., i, 553).—*Methylene*cyclo*heptane* boils at 138—140°, has a sp. gr. 0·824 at 20°, and $n_D = 1·4611$ at 20°. The *glycol*,



$$\left.\begin{array}{l}CH_2\cdot CH_2\cdot CH_2\\ CH_2\cdot CH_2\cdot CH_2\end{array}\right>CH(OH)\cdot CH_2\cdot OH,$$

obtained from it melts at 50—51° and boils at 135—140°; on warming with dilute sulphuric acid, it yields suberanaldehyde, $C_8H_{14}O$, the semicarbazone of which melts at 153—154°.

When hydrochloric acid is removed from the nitrosochloride of methylene*cyclo*heptane, a liquid oxime is obtained which, when warmed with dilute sulphuric acid, yields the *aldehyde*,



$$\left.\begin{array}{l}CH_2\cdot CH_2\cdot CH_2\\ CH_2\cdot CH_2\cdot CH\end{array}\right>C\cdot CHO,$$

the *semicarbazone* of which melts at 203—204°. When oxidised by means of silver oxide, the aldehyde is converted into suberenecarboxylic acid, which melts at 50—51°. H. M. D.

Constitution of Griess' Benzidinedisulphonic Acid. GUSTAV SCHULTZ and W. KOHLHAUS (*Ber.*, 1906, **39**, 3341—3345. Compare Griess, Abstr., 1881, 428; Griess and Duisberg, Abstr., 1890, 57).—Griess' benzidinedisulphonic acid is 4 : 4′-diaminodiphenyl-3 : 3′-disulphonic acid, as on elimination of the amino-groups by diazotisation and treatment of the product with copper powder in alcoholic solution it yields *diphenyl*-3 : 3′-*sulphonic acid*,

$$SO_3H\cdot C_6H_4\cdot C_6H_4\cdot SO_3H,$$

which on fusion with potassium hydroxide is converted into Haeussermann and Teichmann's 3 : 3′-dihydroxydiphenyl (Abstr., 1894, i, 598).

The 3 : 3′-disulphonic acid is obtained as a syrup; it is isolated in the form of its *potassium* salt, $C_{12}H_8O_6S_2K_2,2H_2O$, which crystallises in almost colourless leaflets and is readily soluble in alcohol or water.

Diphenyl-3 : 3′-*disulphonyl chloride*, $C_{12}H_8(SO_2Cl)_2$, crystallises from chloroform in colourless needles, and melts at 127·5—128°; the 3 : 3′-*disulphonamide*, $C_{12}H_8(SO_2\cdot NH_2)_2$, crystallises in stellate aggregates of microscopic needles and melts at 285°; the 3 : 3′-*disulphonanilide*, $C_{12}H_8(SO_2\cdot NHPh)_2$, crystallises in glistening, prismatic, almost colourless prisms and melts at 181·5°. *Methyl diphenyl*-3 : 3′-*disulphonate*, $C_{12}H_8(SO_3Me)_2$, crystallises in white needles and melts at 132·5°. 3 : 3′-Dihydroxydiphenyl crystallises in needles and gives a bluish-violet coloration with ferric chloride. The *dibenzoate*, $C_{12}H_8(OBz)_2$, crystallises in white needles and melts at 92°. G. Y.

Benzylsulphinic Acid and Dibenzyldisulphoxide. EMIL FROMM and JOSÉ DE SEIXAS PALMA (*Ber.*, 1906, **39**, 3308—3317. Compare Otto and Lueders, Abstr., 1880, 811).—Dibenzylsulphone is formed always as an impurity in the preparation of benzylsulphinic acid.

In aqueous solution at the ordinary temperature, sodium benzylsulphonate undergoes slight decomposition, yielding small quantities of benzaldehyde; at higher temperatures, benzoic acid, stilbene, sulphur, and thionessal are formed. Benzylsulphinic acid, prepared by the action of hydrogen sulphide on lead benzylsulphonate, crystallises in needles, is unstable in aqueous solution, being readily hydrolysed to sulphur dioxide and benzaldehyde, and reduces iodine; when treated with methyl iodide and sodium hydroxide, it forms benzylmethylsulphone.

Dibenzyldisulphoxide, $CH_2Ph\cdot SO\cdot SO\cdot CH_2Ph$, is formed by the decomposition of benzylsulphinic acid in aqueous solution. It crystallises in prisms, melts at 108°, is neutral, does not reduce iodine, and when treated with methyl iodide and potassium hydroxide yields benzylmethylsulphone; when boiled with benzyl chloride and sodium hydroxide, it forms dibenzylsulphone and dibenzylsulphoxide.

Benzylsulphonanilide, $CH_2Ph\cdot SO_2\cdot NHPh$, crystallises in white needles melting at 103°; the p-*toluidide*, $C_{14}H_{15}O_2NS$, forms white prisms melting at 113°; the o-*phenetidide*, $C_{15}H_{17}O_3NS$, crystallises in white prisms and melts at 85°.

Sodium and *lead benzylsulphinates* are formed by reduction of benzylsulphonyl chloride with zinc dust and alcohol; they decolorise iodine, but not indigotin, and when boiled with alkyl haloids form benzylalkylsulphones.

Benzylmethylsulphone, $CH_2Ph\cdot SO_2Me$, crystallises in long needles and melts at 127°.

Benzylethylsulphone, $CH_2Ph\cdot SO_2Et$, forms scales or needles and melts at 84°. G. Y.

Oxides of Hydrogen Sulphide. EMIL FROMM and JOSÉ DE SEIXAS PALMA (*Ber.*, 1906, **39**, 3317—3326).—When boiled with sodium hyposulphite and a trace of zinc dust in 30 per cent. aqueous sodium hydroxide, benzyl chloride yields dibenzylsulphone and sodium benzylsulphonate; the hyposulphite reacts therefore as a mixture of a sulphite and a sulphoxylate. The action of sodium hyposulphite on benzyl chloride in 50 per cent. aqueous sodium hydroxide at the ordinary temperature leads to the formation of sodium benzylsulphinate, which is identified by conversion into benzylmethylsulphone (compare preceding abstract).

Zinc dust reacts with sulphuryl chloride in ethereal solution, forming zinc chloride and *zinc sulphoxylate*, $ZnSO_2$, which is converted into dibenzylsulphone when heated with benzyl chloride and 10 per cent. sodium hydroxide; benzylsulphonic acid is not formed, as would be the case were the product of the sulphuryl chloride reaction zinc hyposulphite. The syrupy product obtained on evaporating the ethereal solution of the sulphoxylate reduces indigotin.

Attempts were made to prepare sulphur hydrate, H_2SO, the hypothetical parent substance of the organic sulphoxides, which lies between hydrogen peroxide and hydrogen persulphide.

The action of thionyl chloride on zinc dust leads to the formation of zinc chloride, sulphur dioxide, and sulphur; a sulphoxide is not formed by treating the mixed products with benzyl chloride.

Benzyl disulphide, sulphide, and mercaptan are formed by the action of benzyl chloride on the product of the oxidation of sodium sulphide by hydrogen peroxide.

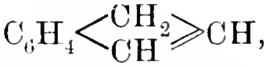
Sodium sulphide is oxidised to only a small extent by the hypochlorite yielding sodium sulphate.

The action of sulphur on potassium hydroxide and treatment of the product with benzyl chloride leads to the formation of thiobenzoic and benzoic acids together with a small amount of benzyl disulphide.

Thiobenzoic acid is oxidised to benzoyl disulphide by potassium ferricyanide in alkaline solution. G. Y.

9-Ethylphenanthrene. ROBERT PSCHORR (*Ber.*, 1906, **39**, 3128—3129).—9-*Phenanthrylmethylcarbinol*, $C_{14}H_9{\cdot}CHMe{\cdot}OH$, resulting from acetaldehyde and 9-bromophenanthrene by the Grignard method, melts at 137° (corr.), and forms an *acetate*, $C_{19}H_{18}O_2$, which melts at 100° and boils at 230—235° under 12 mm. pressure. By distillation with zinc dust, the carbinol yields 9-*ethylphenanthrene*, $C_{16}H_{14}$, which melts at 61—63°, forms a *picrate* melting at 124°, and by oxidation with chromic acid yields phenanthraquinone. C. S.

αγ-Diphenylpropylene. WALTER DIECKMANN and HERMANN KÄMMERER (*Ber.*, 1906, **39**, 3046—3051).—αγ-Diphenylpropylene may be regarded as the open chain analogue of indene,

$C_6H_5{\cdot}CH_2{\cdot}CH{:}CHPh$ 

$$C_6H_4{<}\begin{matrix}CH_2\\CH\end{matrix}{\gg}CH,$$

and accordingly it has been studied with the view of ascertaining how far the capacity for condensation exhibited by indene, fluorene, and *cyclo*pentadiene, and due to the neighbouring ethylene linkings present in these substances, would be recognisable in open chain compounds of similar constitution. The anticipation that the methylene group of αγ-diphenylpropylene would have the same reactivity as that in indene has not been confirmed; the results tend to show that the reactivity of the double linking is increased by the cyclic structure.

αγ-Diphenylpropylene may be prepared from benzylcinnamic acid, obtained by condensing benzaldehyde and dihydrocinnamic acid; this is heated at 100° with a saturated glacial acetic acid solution of hydrogen bromide, when β-bromodibenzylacetic acid is formed, which crystallises from glacial acetic acid in colourless, lustrous needles melting at 191·5°. This acid is converted quantitatively into αγ-diphenylpropylene by warming with excess of aqueous sodium hydroxide. The hydrocarbon thus obtained, which boils at 178—179° under 15 mm. pressure, is a colourless liquid with the fragrant odour of hyacinths; its molecular weight corresponds with the formula $C_{15}H_{14}$. It is probably a stereoisomeride of the solid hydrocarbon (m. p. 57°) obtained by Francis (Trans., 1899, **75**, 869), as the oily hydrocarbon gives a *dibromide* melting at 110°, whilst that derived from the solid hydrocarbon melts at 231°.

The hydrocarbon may be prepared also from αγ-diphenyl-α-propanol or from αγ-diphenyl-β-propanol by conversion into the crude chlorides, which are then heated with diethylaniline, or preferably with pyridine.

αγ-Diphenylpropylene does not condense with ethyl oxalate or diazo-compounds, benzaldehyde or cinnamaldehyde, and it does not develop any coloration with ferric chloride. It is not affected by ethyl nitrite and sodium in dry ethereal solution. When oxidised with permanganate, either in aqueous or acetone solution, it furnishes benzoic, phenylacetic, and benzoylformic acids, the last two being formed in relatively small proportions. G. T. M.

Preparation of Triphenylmethane by the Action of Chloroform or Benzylidene Chloride on Magnesium Phenyl Bromide. ALBERT REYCHLER (*Bull. Soc. chim.*, 1906, [iii], **35**, 737—740).—When chloroform, dissolved in ether, is added to magnesium phenyl bromide dissolved in ether, and the liquid is treated in the usual way, a yield of triphenylmethane equivalent to from 70—80 per cent. of the theoretical is obtained. When chloroform is replaced by benzylidene chloride in this reaction, some tetraphenylmethane is produced in addition to triphenylmethane.

Carbon tetrachloride reacts very violently with magnesium phenyl bromide. Benzenyl trichloride also reacts energetically, forming a crystalline precipitate which, submitted to the usual treatment, yields only a sticky product. Commercial methylene dichloride also reacts with magnesium phenyl bromide, yielding triphenylmethane, but this is probably entirely due to the chloroform present in the commercial article. Chloroform reacts with magnesium ethyl bromide, yielding a colourless precipitate. T. A. H.

Triphenylmethyl. XIV. MOSES GOMBERG and LEE H. CONE (*Ber.*, 1906, **39**, 2957—2970. Compare this vol., i, 414).—The αβββ-Tetraphenylethane prepared by the authors' method was found to be identical in all respects with the product formerly obtained by Hanriot and Saint-Pierre (Abstr., 1889, 882); the pure hydrocarbon may be distilled under reduced pressure, when it boils at 277—280° under 21 mm. pressure.

ααα-Triphenylpropane, formerly obtained as an oil, has now been caused to solidify by sowing with a crystal of the next homologue, triphenylbutane; after crystallisation from methyl alcohol, it melts at 51°.

It was also shown that the oily products obtained by E. and O. Fischer (*Annalen*, 1878, **194**, 259), and by Hanriot and Saint-Pierre (*loc. cit.*), contain crystallisable ααα-triphenylpropane.

ααα-Triphenylbutane, prepared by the interaction of magnesium propyl bromide and triphenylmethyl chloride, propylene and triphenylmethane being obtained as by-products, crystallises from methyl or ethyl alcohol in fine needles or in hexagonal plates; both forms melt at 79°, and the substance boils at 262—265° under 62 mm. pressure.

When *aaa*-triphenylethane is prepared by the interaction of triphenylmethyl chloride and magnesium methiodide, no gaseous olefine was evolved, as in the case of magnesium ethyl or propyl haloid, and the yield of the product was 70 per cent. of the calculated amount.

*aaa-Triphenyl*iso*butane*, produced from magnesium *iso*propyl bromide and triphenylmethyl chloride, boils at 233—234° under 21 mm. pressure, and has not been solidified.

*aaa-Triphenyl*iso*hexane*, prepared from magnesium *iso*amyl bromide and triphenylmethyl chloride, is a viscid, pale yellow, highly refractive oil having an intense blue fluorescence.

The hydrocarbons of this series can all be nitrated with excess of fuming nitric acid until the number of entrant nitro-groups corresponds with the number of phenyl nuclei in the molecule, but in some cases the nitration must be repeated before this result is attained. All the nitrohydrocarbons, with the exception of trinitrotriphenylbutane, give the magenta reaction, and are therefore probably tri-para-derivatives. Two isomeric *tetranitro*-as-*tetraphenylethanes* were obtained, a more soluble substance present only in small quantities and melting at 258°, and the less soluble main product which melts at 269°.

Trinitro-aaa-triphenylpropane, obtained after repeated nitration of the hydrocarbon, crystallises from glacial acetic acid in pale yellow plates and melts at 194—195°.

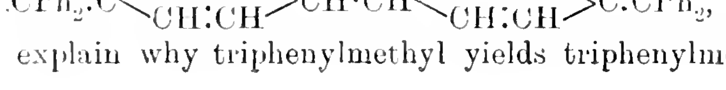
Trinitro-aaa-triphenylbutane crystallises from glacial acetic acid and melts at 191—192°. *Trinitro-aaa-triphenyl*iso*butane* melts at 262—263°. *Trinitro-aaa-triphenyl*iso*hexane* crystallises in prisms, melts at 207—208°, and, like the foregoing nitro-derivative, it dissolves sparingly in glacial acetic acid.

The compound from phenyldiphenylenechloromethane, described in the last communication as a hydrocarbon (this vol., i, 414), is now found to be *phenylfluorene peroxide*, $\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!\!>CPh\cdot O\cdot O\cdot CPh<\!\!\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}$; this substance separates from benzene in transparent, tabular crystals containing $2C_6H_6$, which evolve the solvent on exposure to air and then melt at 193°. This peroxide may also be prepared by shaking a benzene solution of phenyldiphenylenechloromethane with 5 per cent. aqueous sodium peroxide containing some acetic acid. G. T. M.

Triphenylmethyl. XV. Moses Gomberg and Lee H. Cone (*Ber.*, 1906, 39, 3274—3297. Compare Abstr., 1905, i, 641; Heintschel, Abstr., 1903, i, 243; Jacobson, Abstr., 1905, i, 186).—The present views as to the constitution of triphenylmethyl are (1) that it contains a tervalent carbon atom, (2) that it is hexaphenylethane, and (3) that it is a quinonic substance.

(2) This view can be no longer upheld, as tetraphenyl- and pentaphenylethane have been prepared and found to be stable substances.

(3) Heintschel's formula



$$CPh_2\!:\!C<\!\begin{matrix}CH\!:\!CH\\CH\!:\!CH\end{matrix}\!>CH\cdot CH<\!\begin{matrix}CH\!:\!CH\\CH\!:\!CH\end{matrix}\!>C\!:\!CPh_2,$$

does not explain why triphenylmethyl yields triphenylmethyl iodide when treated with iodine. Jacobson's formula has been discussed previously (Abstr., 1905, i, 641).

The following halogen substitution products of triphenylmethyl have been prepared by Friedel-Craft's synthesis or by Grignard's reaction (compare Gomberg, Abstr., 1904, i, 489).

p-Chlorotriphenylchloromethane, prepared from *p*-chlorobenzophenone and magnesium phenyl bromide, reacts with *p*-toluidine, forming p-*chlorotriphenylmethyl*-p-*toluidine*, $C_{26}H_{22}NCl$, melting at 131°. The *carbinol*, $OH\cdot CPh_2\cdot C_6H_4Cl$, formed by hydrolysis of the chloride with sulphuric acid, crystallises with difficulty and melts at 85°. *p*-Bromotriphenylchloromethane, prepared from *p*-bromobenzophenone and magnesium phenyl bromide, melts at 114°. The *carbinol* crystallises slowly and melts at 74°. *p*-Iodotriphenylchloromethane, prepared from benzophenone dichloride, iodobenzene, and aluminium chloride, melts at 123°.

Di-p-*chlorotriphenylchloromethane*, $CPhCl(C_6H_4Cl)_2$, prepared from di-*p*-chlorobenzophenone and magnesium phenyl bromide and purified by means of its green, iridescent *ferrichloride*, $C_{19}H_{13}Cl_3,FeCl_3$, separates from light petroleum in opaque, crystalline aggregates and melts at 87°. The corresponding *di*-p-*bromo*-compound melts at 100°; the *carbinol* crystallises from light petroleum in opaque masses and melts at 110°.

2 : 4′ : 4″-*Trichlorotriphenylchloromethane*, $CCl(C_6H_4Cl)_3$, prepared together with a small quantity of tri-*p*-chlorotriphenylchloromethane, which is more soluble in light petroleum than is the 2 : 4′ : 4″-compound, or by the action of carbon tetrachloride and aluminium chloride on chlorobenzene at 60—70°, or from magnesium *p*-chlorophenyl iodide and 2 : 4′-dichlorobenzophenone, forms large crystals and melts at 153°. The corresponding *carbinol*, $OH\cdot C(C_6H_4Cl)_3$, crystallises from light petroleum, melts at 111·5—112·5°, and on oxidation with chromic acid in glacial acetic acid solution yields 4 : 4′-dichlorobenzophenone. 2 : 4′ : 4″-*Trichlorotriphenylmethane*, $CH(C_6H_4Cl)_3$, prepared by reduction of the carbinol or its chloride with zinc dust and glacial acetic acid, melts at 106°. 2 : 4′ : 4″-*Trichlorotriphenylmethyl ethyl ether*, $OEt\cdot C(C_6H_4Cl)_3$, prepared by treating the chloride with sodium ethoxide, crystallises slowly and melts at about 40°.

Tri-p-*bromotriphenylchloromethane*, $CCl(C_6H_4Br)_3$, is the main product of the action of carbon tetrachloride and aluminium chloride on bromobenzene; it crystallises in thin, hexagonal prisms, melts at 153°, and gives an orange-red coloration on addition of molecular silver to its solution in benzene. The *carbinol* crystallises in clear, transparent, hexagonal prisms and melts at 131°. The *ethyl ether*,

$$OEt\cdot C(C_6H_4Br)_3,$$

melts at 206°.

2 : 4′ : 4″-*Tribromotriphenylchloromethane*, $C_{19}H_{12}ClBr_3$, formed in small amount from carbon tetrachloride and bromobenzene, or by diazotation of pararosaniline, decomposition of the product with cuprous bromide, and treatment with hydrogen chloride in benzene solution, crystallises in small cubes, melts at 154—155°, and gives an intense purple colour with molecular silver in benzene solution; the *carbinol* melts at 134°; the *ethyl ether*, $OEt\cdot C(C_6H_4Br)_3$, melts at 75—80°.

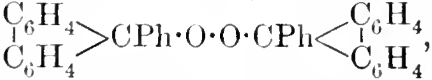
The action of molecular silver and air on the halogen-substituted triphenylchloromethanes in benzene solution leads to the formation of the corresponding peroxides, $CR_3\cdot O\cdot O\cdot CR_3$ (compare Gomberg, *loc. cit.*). The position of the substituting halogen atoms only is given, the temperatures are melting points: o-*monochloro-*, 150°; m-*monobromo-*, 170°: *di*-p-*bromo-*, 174°; 2 : 4′ : 4″-*trichloro-*, 140°; *tri*-p-*chloro-*, 182°; *tri*-p-*bromo-*, 192°; 2 : 4′ : 4″-*tribromo-*, 153°.

These peroxides are obtained also in yields varying from 50—60 to 3—4 per cent. by the action of sodium peroxide on the carbinol chlorides.

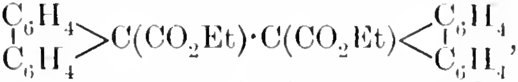
Even after some years triphenylmethyl does not lose its power of absorbing oxygen and forming peroxides. In the action of molecular silver and air on the above substituted triphenylchloromethanes, the first product must be the unsaturated substance, the substituted triphenylmethyl, which in the second stage of the reaction absorbs oxygen.

A number of experiments are described to show that if the chloromethane is shaken for a short time with molecular silver and immediately exposed to air, the peroxide is formed, but if the shaking be too prolonged the molecular silver attacks the halogen atoms in the benzene nuclei. The velocity of the reaction varies with the number and nature of the halogens present. Connected with this are (1) the coloration formed when the molecular silver is added to the chloromethane in benzene solution, (2) the amount of halogen removed from the benzene nuclei, and (3) the nature of the resulting product. The results of determinations of (1) and (2) are given in tables. The *product* obtained on prolonged shaking of 2 : 4′ : 4″-trichlorotriphenylchloromethane with molecular silver and benzene is an amorphous, light yellow glass which is soluble in benzene or ether. Molecular weight determinations by the cryoscopic method give results which point to the removal of the chlorine being accompanied by the union of two of the triphenylmethyl molecules. This agrees better with Jacobson's than with Heintschel's formula for triphenylmethyl.

The authors conclude that the highly coloured, unstable derivatives of triphenylmethyl must be closely related to the stable triphenylmethane dyes. G. Y.

Removal of Chlorine from *α*-Chlorinated Fluorene Derivatives. HERMANN STAUDINGER (*Ber.*, 1906, **39**, 3060—3062. Compare Gomberg, this vol., i, 414).—*Phenyldiphenylenemethyl* [9-*phenylfluoryl*] *peroxide*,  $\begin{array}{c}C_6H_4\\|\\C_6H_4\end{array}\!\!>CPh\cdot O\cdot O\cdot CPh<\!\!\begin{array}{c}C_6H_4\\|\\C_6H_4\end{array}$, separates after one to two days, when an ethereal solution of 9-chloro-9-phenylfluorene (obtained conveniently by saturating the carbinol in glacial acetic acid with hydrogen chloride; compare Kliegl, Abstr., 1905, i, 187) is treated with amalgamated zinc in the presence of air and absence of moisture. It separates from benzene in crystals containing $2C_6H_6$, and melts at 194°.

9-Chlorofluorene under similar conditions yields *bisdiphenylene-ethane*, which melts at 239°.

Ethyl diphenylenechloroacetate, obtained from phosphoric chloride and ethyl diphenyleneglycollate, melts at 46—47°, does not react with zinc in ethereal solution, but with molecular silver yields *ethyl bisdiphenylenesuccinate*,  $\begin{array}{c}C_6H_4\\ |\\ C_6H_4\end{array}>C(CO_2Et)\cdot C(CO_2Et)<\begin{array}{c}C_6H_4\\ |\\ C_6H_4\end{array}$, which separates from chloroform or benzene in large crystals and melts at 168—169°. C. S.

Dibenzylnaphthalene. JOSSIF J. VON BOGUSKI (*Ber.*, 1906, **39**, 2866—2869).—When naphthalene and benzyl chloride are boiled for some time in the presence of a small quantity of aluminium powder, the products are α- and β-benzylnaphthalene and a *dibenzylnaphthalene*, $C_{24}H_{20}$. The last compound can be isolated from the fraction boiling at 250—273° under 33 mm. pressure. It forms slender, colourless, triclinic needles, melts at 146·5°, and dissolves in hot alcohol and in most organic solvents. J. J. S.

Preparation of a 3 : 4-Dichloroanilinesulphonic Acid. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 172461).—3 : 4-Dichloroaniline, when heated with a molecular proportion of sulphuric acid at 215°, yields a sulphonic acid which is probably 3 : 4-*dichloroaniline*-6-*sulphonic acid*. This substance is a white powder, soluble in 200 parts of hot and 1000 parts of cold water, which furnishes a sparingly soluble, colourless diazo-derivative and well-defined *sodium* salt, crystallising in large, lustrous leaflets. The *potassium* salt also crystallises readily; the *barium*, *zinc*, and *copper* salts are also soluble. G. T. M.

Reduction of Nitro-compounds by Alkaline Solutions of Stannous Oxide. HEINRICH GOLDSCHMIDT and MORITZ ECKARDT (*Zeit. physikal. Chem.*, 1906, **56**, 385—452. Compare Goldschmidt and Ingebrechtsen, Abstr., 1904, ii, 608; Goldschmidt and Sunde, this vol., i, 734).—The relation of the free to the combined alkali in alkaline solutions of stannous hydroxide has been ascertained by determining the solubility of the hydroxide in sodium hydroxide solutions of different strengths. From these determinations it appears that stannous hydroxide acts as a monobasic acid (compare Hantzsch, Abstr., 1902, ii, 395), and that in sodium hydroxide solution it exists chiefly as the salt SnO_2HNa. A saturated solution of stannous hydroxide in pure water is found to contain 0·0000135 gram-mol. per litre, and when this result is combined with the values for the solubility in alkaline solutions, it appears that the affinity constant of stannous hydroxide as an acid is of the same order as that of phenol. The view that stannous hydroxide in sodium hydroxide solutions exists chiefly as the salt SnO_2HNa was confirmed by observing the catalytic effect of these solutions on the change of diacetonealcohol into acetone (see Koelichen, Abstr., 1900, ii, 395). The stannous solutions were prepared by electrolysing a solution of sodium hydroxide with a tin anode, and the course of the change of the diacetonealcohol into acetone was followed in a dilatometer. Similar experiments indicate that, when alkaline stannous hydroxide solutions are oxidised, the stannate produced contains sodium and tin in the atomic ratio 2 : 1.

The character of the reduction by alkaline stannous hydroxide solutions varies very much from one nitro-compound to another. Of the substances studied there are four which react with 3 molecules of stannous hydroxide, and yield amino-compounds directly: these are *o*- and *p*-nitrophenols and *o*- and *p*-nitroanilines. Other substances, namely, *m*-nitrophenol, *m*-nitroaniline, the three nitrobenzoic acids, the three nitrobenzenesulphonic acids, *p*-nitrotoluenesulphonic acid, and *o*-nitrobenzaldehyde, react with 2 molecules of stannous hydroxide. There is, however, further diversity, for whilst of the latter list *o*-nitrobenzoic acid and *o*-nitrobenzaldehyde lead to a hydroxylamine derivative as the end-product of the reaction, the others yield azo- and azoxy-compounds.

As regards the rate of reduction, the phenomena are simplest when the concentrations of tin and soda are low, and in these cases the velocity coefficient calculated for an equation of the second order is fairly constant. It is probable that the ion $SnHO'_2$ is the effective agent in the reduction, and that the nitro-compound is first reduced to a nitroso-compound, which in its turn is further reduced with infinitely great velocity. The value of the velocity coefficient rises markedly as the soda concentration is increased. This increase may be accounted for if it is assumed that in the more concentrated soda solutions disodium stannite is present.

In the following table are compared the values of the velocity coefficient of reduction for various nitro-compounds, (*a*) with alkaline stannous hydroxide solutions, (*b*) with stannous chloride and hydrochloric acid:

		Ortho.	Meta.	Para.
Nitroaniline	*a*	20	150	13·4
	b	0·655	0·175	0·10
Nitrophenol	*a*	5·72	40	1·57
	b	0·022	0·023	0·0022
Nitrobenzoic acid	*a*	97	130	226
	b	0·122	0·064	—
Nitrobenzenesulphonic acid	*a*	584	273	484
	b	0·052	0·073	0·129
Nitrobenzaldehyde	*a*	1030	—	—
	b	0·245	0·078	—

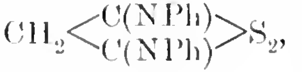
J. C. P.

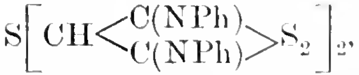
Sulphur Derivatives of the Anilides of Malonic, Succinic, and Phenylacetic Acids and their Transformation Products.

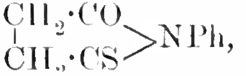
ARNOLD REISSERT and ARNOLD MORÉ (*Ber.*, 1906, **39**, 3298—3308. Compare Reissert, Abstr., 1904, i, 990).—The action of phosphorus pentasulphide on malonanilide in boiling toluene solution in a reflux apparatus leads to the formation of *dithionmalonanilide*,

$$CH_2(CS{\cdot}NHPh)_2,$$

which crystallises from alcohol in yellow needles, melts at 149°, and is soluble in aqueous sodium hydroxide, but is insoluble in aqueous sodium carbonate. The *dithion-o-toluidide*, $CH_2(CS{\cdot}NH{\cdot}C_7H_7)_2$, prepared in the same manner from malon-*o*-toluidide, crystallises in yellow needles and melts at 122—123°. The *dithion-p-toluidide*, $C_{17}H_{18}N_2S_2$, melts at 145°.

When shaken with cold concentrated sulphuric acid, dithionmalonanilide yields *dehydrodithionmalonanilide*,  $CH_2<\begin{smallmatrix}C(NPh)\\C(NPh)\end{smallmatrix}>S_2$, which crystallises in matted, yellow needles, melts at 154—155°, and is insoluble in aqueous alkali hydroxides.

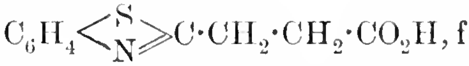
The action of hot dilute sulphuric acid on dithionmalonanilide leads to the formation of *dehydrodithionmalonanilide sulphide*,  $S\left[CH<\begin{smallmatrix}C(NPh)\\C(NPh)\end{smallmatrix}>S_2\right]_2$, which crystallises in golden leaflets, melts and decomposes at 197°, and, when boiled with concentrated aqueous sodium hydroxide, yields a small amount of dithionmalonanilide, together with a *substance*, $C_{30}H_{22}N_4S_5$, melting at 210°.

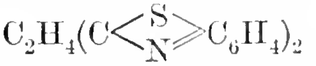
Thionsuccinanil,  $\begin{smallmatrix}CH_2\cdot CO\\|\\CH_2\cdot CS\end{smallmatrix}>NPh$, is formed in only small amount by the action of phosphorus pentasulphide on succinanil, but in good yields by boiling methyl succinanilate with phosphorus pentasulphide in toluene solution. It separates from alcohol in stout, yellow crystals, melts at 116—117°, forms sodium sulphide when heated with aqueous sodium hydroxide, and when treated with cold alcoholic sodium hydroxide yields *sodium thionsuccinanilate*. The free *acid*,

$$NHPh\cdot CS\cdot CH_2\cdot CH_2\cdot CO_2H,$$

melts at 106—107°.

Methyl succinanilate is prepared best by boiling succinanil with concentrated sulphuric acid and methyl alcohol.

Benzothiazole-2-propionic acid,  $C_6H_4<\begin{smallmatrix}S\\N\end{smallmatrix}>C\cdot CH_2\cdot CH_2\cdot CO_2H$, formed by shaking thionsuccinanilic acid with potassium ferricyanide in alkaline solution, crystallises in stout, white needles, melts at 108—109°, and is soluble in most organic solvents or dilute mineral acids. The *ammonium* and *silver* salts are described; the *methyl* ester, $C_{11}H_{11}O_2NS$, crystallises in soft, slender needles and melts at 57—58°; the *anilide*, $C_7H_4NS\cdot CH_2\cdot CH_2\cdot CO\cdot NHPh$, forms colourless needles and melts at 149°; the *thionanilide*, $C_7H_4NS\cdot CH_2\cdot CH_2\cdot CS\cdot NHPh$, formed by the action of phosphorus pentasulphide on the anilide in boiling xylene solution, crystallises in stout, yellow needles and melts at 127°.

s-Dibenzothiazylethane,  $C_2H_4(C<\begin{smallmatrix}S\\N\end{smallmatrix}>C_6H_4)_2$ (Hofmann, Abstr., 1880, 388), is formed by oxidation of the preceding substance by means of potassium ferricyanide in alkaline solution.

Thionphenylacetoanilide, $C_{14}H_{13}NS$, prepared by the action of phosphorus pentasulphide on phenylacetanilide in boiling toluene solution, crystallises in long, soft, silky, yellow needles, melts at 88°, and is readily soluble in aqueous alkali hydroxides. G. Y.

Adipanilide. EYVIND BÖDTKER (*Ber.*, 1906, **39**, 2765).—*Adipanilide*, $C_{18}H_{20}O_2N_2$, obtained by heating the acid and aniline at 190° for eight hours, crystallises from hot alcohol in glistening plates or feathery needles, melts at 240° (corr.), and dissolves in most organic solvents with the exception of ether. J. J. S.

ω-Sulphonic Acids and ω-Cyanides of Aromatic Amines. HANS BUCHERER and ARTHUR SCHWALBE (*Ber.*, 1906, **39**, 2796—2813).—Sodium methylaniline-ω-sulphonate [*anilinomethanesulphonate*], $NHPh\cdot CH_2\cdot SO_3Na$, is obtained quantitatively by the interaction of formaldehyde bisulphite and aniline and converted into cyanomethylaniline by the action of potassium cyanide; the effect of steam, temperature, acids, and nitrous acid on the yields obtained in this reaction have been investigated. *Sodium monomethyl*-p-*toluidino-ω-sulphonate,* $C_7H_7\cdot NH\cdot CH_2\cdot SO_3Na$, crystallises in large platelets; the sodium salt of the o-*toluidine* derivative gives a flocculent precipitate, and the *barium* salt crystallises in plates. *Sodium monomethyl*-o-*anisidine-ω-sulphonate,* $OMe\cdot C_6H_4\cdot CH_2\cdot SO_3Na$, crystallises in thick, voluminous platelets, the decomposition with potassium cyanide begins at 90°, and the *ω-cyanomethyl*-o-*anisidine* crystallises in glistening prisms melting at 68°. *Sodium monomethyl*-p-*nitroanilino-ω-sulphonate* separates in yellow needles and does not yield the nitrile.

The *disodium* salt of dimethyl-*m*-tolylene-2:4-diaminedi-ω-sulphonic acid crystallises in needles grouped in stellar aggregates; *di-ω-cyanodimethyltolylene*-2:4-*diamine* forms faintly yellow-coloured needles melting at 207°. *Sodium monomethyltolylene*-2:4-*diamine-ω-sulphonate* crystallises in diagonally-crossed needles, the *nitrile* separates as an oil. *Sodium dimethyl*-p-*phenylenediaminedi-ω-sulphonate* crystallises in rhombic plates, *ω-cyanomonomethyl*-p-*phenylenediamine* crystallises in plates melting at 168°; the *sodium* salt of the corresponding *sulphonate* forms minute needles. *Sodium dimethylbenzidinedi-ω-sulphonate* separates in broad needles which are not altered by boiling with water; *di-ω-cyanodimethylbenzidine* melts at 241—242°; *sodium monomethylbenzidine-ω-sulphonate* separates in bundles of needles, whilst the corresponding *ω-cyanomonomethylbenzidine* crystallises in platelets melting at 142—144° and forms a sparingly soluble *diazo*-compound which gives rise to red dyes.

ω-Cyanomethylanthranilic acid is a light yellow compound melting at 184°. *Sodium methyl-α-naphthylamine-ω-4-disulphonate* crystallises in prisms, *sodium-ω-cyanomethylnaphthionic acid* crystallises in well-formed plates which melt and become brown at 258°. *Sodium methyl-α-naphthylamine-ω-sulphonate* is a colourless, crystalline powder which becomes reddish-violet when exposed to damp air, *ω-cyanomethyl-α-naphthylamine* crystallises in long needles melting at 92°, whereas Knoevenagel (Abstr., 1904, i, 989) found 44—45°. The corresponding *ω-cyanomethyl-β-naphthylamine* melts at 102—104°.

Sodium methylethylaniline-ω-sulphonate crystallises in thick plates and yields 75 per cent. of the nitrile, decomposing with potassium cyanide at 60°. Aniline and benzaldehydebisulphite condense to the sodium benzylaniline-ω-sulphonate described by Eibner (Abstr., 1901, i, 376). *ω-Cyanobenzyl*-o-*anisidine* forms minute, glistening prisms melting at 73°. E. F. A.

Action of Bromine on Dimethylaniline. II. C. LORING JACKSON and LATHAM CLARKE (*Amer. Chem. J.*, 1906, **36**, 409—414. Compare Abstr., 1905, i, 768).—A repetition of the experiments described in the earlier paper (*loc. cit.*) has shown that a mixture of dimethylaniline, bromine, and chloroform may give two entirely different products even when there is no apparent difference in the conditions of the reaction; thus sometimes the additive compound, $C_6H_5Br_2{\cdot}NMe_2$, is produced, whilst at other times substitution occurs with formation of the compound $C_6H_4Br{\cdot}NMe_2,HBr,Br$, described by Fries (Abstr., 1904, i, 571). E. G.

A New Method of Preparing Aromatic Amines. FRANZ SACHS [and in part E. APPENZELLER, VIKTOR HEROLD, B. MYLO, KURT SCHÄDEL, and THEODOR SUTTER] (*Ber.*, 1906, **39**, 3006—3028).—In attempting to obtain evidence of the existence of the heteronucleal 2:6-naphthaquinone or its derivatives the author was led to a new method of preparing 5-amino-β-naphthol, which consisted in heating sodium β-naphthol-6-sulphonate with sodamide for forty minutes at 230—240° in a copper vessel fitted with a stirrer. In this way the sulphonic residue was eliminated and the NH_2 group introduced into a different position in the ring, and a yield of 51 per cent. of the product was obtained. The process was then extended to other derivatives of the aromatic hydrocarbons.

The sodium salts of benzenesulphonic and naphthalene-β-sulphonic acids when fused with sodamide furnished 30 and 32 per cent. of aniline and β-naphthylamine respectively. β-Naphthol-7-sulphonic acid gave rise to a mixture of isomeric aminonaphthols, in which 7-amino-β-naphthol and 5-amino-β-naphthol were identified. β-Naphthol-8-sulphuric acid also furnished a mixture of isomerides, which were partially separated by means of their benzoyl derivatives.

The basic salt of β-naphthol-1-sulphonic acid yielded a homogeneous product which, however, has not been identified with any of the known aminonaphthols.

α-Naphthol-5-sulphonic acid, when subjected to the sodamide fusion, furnished 5-amino-α-naphthol, which was characterised by the formation of a blue azo-dye with α-diazonaphthalene-4-sulphonic acid. 8-Amino-α-naphthol itself was not isolated from the sodamide fusion of α-naphthol-8-sulphonic acid, but was separated from the tarry by-products only in the form of its picrate.

Sodium anthraquinone-β-sulphonate, when fused with a mixture of sodamide and naphthalene, yielded anthranol, anthraquinone, and a base melting at 255°, which, although having the composition and molecular complexity of an aminoanthraquinone, is not identical with either α- or β-aminoanthraquinone.

β-Naphthol, when fused with sodamide and excess of naphthalene, yielded principally 6-amino-β-naphthol, together with small amounts of 7-amino-β-naphthol and the isomeride derived from β-naphthol-1-sulphonic acid; traces of naphthylenediamines were also discernible in the products of fusion.

α-Naphthol gave 5-amino-α-naphthol at 190°, at higher temperatures 1:5-naphthylenediamine results.

α-Naphthylamine, sodamide, and naphthalene, when fused for thirty minutes at 230°, give a 47 per cent. yield of pure 1:5-naphthylenediamine; hydrogenated naphthalenes are produced when the heating is prolonged.

β-Naphthylamine under similar conditions gives 2 : 5-naphthylenediamine and a trace of an ortho-diamine, probably 2 : 3-naphthylenediamine.

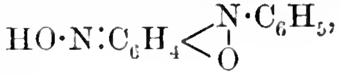
When naphthalene, phenol, and sodamide are fused at 200—220°, amino-groups are introduced into the naphthalene nucleus, and α-naphthylamine and 1 : 5-naphthylenediamine are produced, and similar results are obtained when resorcinol or sulphanilic acid are employed in the fusion instead of phenol.

The following substances were employed in characterising the aminonaphthols: dibenzoyl-1-amino β-naphthol, silky needles, melting point 235·5° (compare Trans., 1889, **55**, 121); N-*benzoyl-3-amino-β-naphthol*, hexagonal plates, melting point 233·5°; *dibenzoyl-4-amino-β-naphthol*, rhombic plates, melting at 309—310°; *dibenzoyl-5-amino-β-naphthol*, white needles, melting at 223°; N-*benzoyl-5-amino-β-naphthol*, white needles, melting at 152°; *diacetyl-5-amino-β-naphthol*, melting at 187°; *acetyl-5-amino-2-methoxynaphthalene*, felted needles, melting at 140°; 5 *amino-β-naphthol picrate*, yellow needles, melting point 183°; *dibenzoyl-6-amino-β-naphthol*, prisms, melting at 233·5°; *dibenzoyl-7-amino-β-naphthol*, white needles, melting at 187·5°; *dibenzoyl-8-amino-β-naphthol*, white prisms, melting at 208°; *dibenzoyl-4-amino α-naphthol*, rhombic crystals, melting at 215°; *dibenzoyl-5-amino-α-naphthol*, rhombic plates, melting at 276°.

The following derivatives of 1 : 8-naphthylenediamine were prepared: *dibenzoyl-1 : 8-naphthylenediamine*, needles, melting at 311—312°; *ethylidene-1 : 8-naphthylenediamine*, crystallising from dilute alcohol in green needles and decomposing at 210°.

2 : 6-Dihydroxynaphthalene, when treated with oxidising agents such as ferric chloride, potassium dichromate, ammonium persulphate, manganese dioxide and sulphuric acid, potassium permanganate and potassium hypobromite, furnishes yellowish-white precipitates which dissolve in aqueous alkalis to a green solution; the analytical data and molecular determinations of their oxidation products agree approximately with the formula $(C_{10}H_5O_2)_4$. G. T. M.

Substituted Diphenylhydroxylamines. HEINRICH WIELAND and STEPHAN GAMBARJAN (*Ber.*, 1906, **39**, 3036—3042. Compare this vol., i, 453).—*p*-Nitrosodiphenylhydroxylamine, $NO\cdot C_6H_4\cdot N(OH)\cdot C_6H_5$, prepared by Bamberger's method from nitrosobenzene and cold concentrated sulphuric acid, was converted into its *methyl ether* by shaking with methyl sulphate and dilute aqueous sodium hydroxide; this melted at 137—138° without decomposition; it is soluble in all the organic media. It is markedly basic, and when warmed with moderately concentrated sulphuric acid it undergoes hydrolysis and nitrosobenzene is produced. On reduction either with zinc dust and acetic acid or alcoholic hydrogen sulphide, it yields *p*-aminodiphenylamine.

These reactions are most readily explained on the supposition that *p*-nitrosodiphenylhydroxylamine is a pseudo-acid, which, on the formation of a salt, assumes the quinonoid *aci*-form,  $HO\cdot N{:}C_6H_4{<}\overset{N\cdot C_6H_5}{\underset{O}{|}}$, and yields a methyl ether having a similar constitution.

2 : 4-*Dinitrodiphenylhydroxylamine*, $C_6H_5{\cdot}N(OH){\cdot}C_6H_3(NO_2)_2$, is formed together with dinitrodiphenylamine and aniline when 1-bromo-2 : 4-dinitrobenzene and phenylhydroxylamine are heated in alcoholic solution in a reflux apparatus. It separates from benzene in flattened, orange-coloured needles melting and decomposing at 114—115°, is readily soluble in most organic media excepting petroleum, and is scarcely soluble in water. In aqueous solutions of ammonia or the alkali hydroxides, it furnishes soluble, brownish-red salts corresponding with the quinonoid *aci*-form. On reduction with zinc dust and acetic acid, diaminodiphenylamine is produced. G. T. M.

Benzoyl-*p*-bromophenylcarbamide: a By-product in the Preparation of Benzoylbromoamide. FORRIS J. MOORE and A. M. CEDERHOLM (*J. Amer. Chem. Soc.*, 1906, **28**, 1190—1198).—When benzoylbromoamide is prepared by Hoogewerff and van Dorp's method (Abstr., 1889, 981), it is liable to contain as much as 10 per cent. of benzoyl-*p*-bromophenylcarbamide.

Benzoyl-p-*bromophenylcarbamide*, $C_6H_4Br{\cdot}NH{\cdot}CO{\cdot}NHBz$, crystallises in silky needles, melts at 230° in a closed tube, decomposes at 232°, and is soluble in glacial acetic acid and insoluble in water or ether. The compound can be synthesised (1) by the action of phenylcarbamide on benzoylbromoamide in benzene solution, (2) by the action of *p*-bromophenylcarbimide on benzoylbromoamide in alkaline solution, (3) by heating a mixture of *p*-bromophenylcarbimide and benzamide, and (4) by the action of benzoylbromoamide on benzoylphenylcarbamide in benzene solution.

The production of benzoyl-*p*-bromophenylcarbamide in the preparation of benzoylbromoamide is regarded as due to the formation of benzoylphenylcarbamide in the course of the reaction and its subsequent bromination by the benzoylbromoamide itself. E. G.

Action of Bases on Thiocarbamides. REINHOLD VON WALTHER and A. STENZ (*J. pr. Chem.*, 1906, [ii], **74**, 222—231. Compare Abstr., 1900, i, 569).—The action of ammonium acetate on *s*-diphenylthiocarbamide in glacial acetic acid solution on the water-bath leads to the formation of hydrogen sulphide and *s*-diphenylcarbamide, but in alcoholic solution to the formation of phenylthiocarbamide.

When heated with hydroxylamine hydrochloride in acetic acid solution, *s*-diphenylthiocarbamide yields *s*-diphenylcarbamide, aniline, and carboxyl sulphide; phenyloxythiocarbamide, formed as an intermediate product in this reaction, yields *s*-diphenylcarbamide, aniline, and carbonyl sulphide when heated with glacial acetic acid.

When heated with hydroxylamine in alcoholic solution, *s*-diphenylthiocarbamide forms sulphur and aniline.

s-Diphenylcarbamide, acetanilide, and hydrogen sulphide are formed by heating guanidine with *s*-diphenylthiocarbamide in glacial acetic acid solution (compare Bamberger, Abstr., 1881, 43).

The action of hydrazine on *s*-diphenylthiocarbamide in alcoholic solution on the water-bath leads to the formation of hydrazodicarbonthiophenylamide, together with small amounts of hydrogen sulphide and a *substance*, $C_{14}H_{12}N_4S$, which is obtained also by boiling

2 mols. of *s*-diphenylthiocarbamide with 1 mol. of hydrazine in glacial acetic acid solution; it crystallises in yellow leaflets and melts at 237°.

When boiled with *o*-toluidine in alcoholic solution for one hour, or in glacial acetic acid solution for ten minutes, *s*-diphenylthiocarbamide forms aniline and *ab*-phenyl-*o*-tolylthiocarbamide; *ab*-phenyl-*m*-tolylthiocarbamide is formed in the same manner from *s*-diphenylthiocarbamide and *m*-toluidine.

ab Phenyl-*p*-tolylthiocarbamide melts at 141°; the substance melting at 158° (*loc. cit.*) is a mixture of homologous thiocarbamides (compare Kjellin, Abstr., 1903, i, 287; Hugershoff, *ibid.*, 477). This mixture is formed also by the action of *p*-toluidine on phenylthiocarbimide.

When heated with phenylhydrazine in alcoholic or acetic acid solution, or without a solvent, *s*-diphenylthiocarbamide forms diphenylthiosemicarbazide melting at 177° (Walther, Abstr., 1896, i, 534).

1-Phenyl-4-*p*-tolylthiosemicarbazide formed by heating di-*p*-tolylthiocarbamide, or *ab*-phenyl-*p*-tolylthiocarbamide with phenylhydrazine in glacial acetic acid solution, melts at 165° and remains unchanged when heated with alcoholic hydrogen chloride (compare Marckwald, Abstr., 1893, i, 26; 1899, i, 503).

1-Phenyl-4-*o*-tolylthiosemicarbazide formed from *ab*-phenyl-*o*-tolylthiocarbamide, melts at 156°.

Diphenylmethylthiosemicarbazide is obtained by heating *s*-diphenylthiocarbamide with phenylmethylhydrazine in glacial acetic acid solution; 1 : 4-diphenylthiosemicarbazide is formed by heating guanylphenylthiocarbamide with an excess of phenylhydrazine. G. Y.

Behaviour of Carboxylic Acids towards Phenylcarbimide.

Walter Dieckmann and Fritz Breest (*Ber.*, 1906, **39**, 3052—3055).—The action of phenylcarbimide on carboxylic acids leads to the formation of mixed anhydrides, RCO·O·CO·NHPh, of phenylcarbamic acid and the corresponding carboxylic acid.

Lævulic acid and phenylcarbimide when mixed in molecular proportions yield a colourless, crystalline mass of the mixed *anhydride*, $CMeO\cdot CH_2\cdot CH_2\cdot CO\cdot O\cdot CO\cdot NHPh$. This substance, when freshly prepared, is readily soluble in dry ether; it is, however, somewhat unstable and is decomposed into lævulic acid and diphenylcarbamide by water, and by cold alcohol into lævulic acid and ethyl phenylcarbamate. Ammonia resolves it into lævulic acid and diphenylcarbamide. The anhydride evolves carbon dioxide slowly at the ordinary temperature, rapidly at 100°, diphenylcarbamide and lævulic anhydride being produced; some angelicalactone was also noticed. Ethyl lævulate does not interact with phenylcarbimide.

β-Benzoylpropionic acid forms a similar mixed anhydride with phenylcarbimide. The additive compound from phenylacetic acid and phenylcarbimide is a colourless, crystalline mass, which is decomposed by water, alcohol, or ammonia. The spontaneous decomposition of this product at the ordinary temperature is complete within forty-eight hours, carbon dioxide is evolved, and the residue consists chiefly of phenylacetanilide together with some diphenylcarbamide and phenylacetic anhydride.

Acetic acid and phenylcarbimide combine with generation of heat to form an additive compound, which is decomposed in about twenty-four hours at the ordinary temperature into carbon dioxide and acetanilide, together with a certain amount of diphenylcarbamide and acetic anhydride.

Dihydrocinnamic acid and phenylcarbimide furnish a crystalline additive compound which slowly evolves carbon dioxide at the ordinary temperature. At 100° it decomposes into carbon dioxide, diphenylcarbamide, and dihydrocinnamic anhydride, whilst at 180° dihydrocinnamanilide is the chief product. Water, alcohol, and ammonia decompose the mixed anhydride regenerating dihydrocinnamic acid.

The additive products from cinnamic and benzoic acids have similar properties. G. T. M.

Ozonides of Hydro-aromatic Compounds and the Stability of Different Ring Systems. Carl D. Harries and Heinrich Neresheimer (*Ber.*, 1906, **39**, 2846—2850. Compare Abstr., 1904, i, 361, this vol., 261).—*Tetrahydrobenzeneozonide*, $C_6H_{10}O_3$, obtained by passing ozone into a chloroform solution of the unsaturated hydrocarbon, forms elastic lumps sparingly soluble in all ordinary solvents. When boiled for some time with water it yields a considerable amount of *n*-adipic acid and a small amount of the corresponding aldehyde.

m-Dihydro-xylene (Verley, Abstr., 1898, i, 557) yields a *diozonide* $C_6H_6Me_2O_6$, which, after repeated solution in ethyl acetate and precipitation with light petroleum, forms a water-clear syrup with a characteristic odour. It dissolves readily in most organic solvents, is comparatively stable, but occasionally explodes with great violence. When reduced it yields lævulinaldehyde, and hence the hydrocarbon is probably 1 : 3-dimethyl-$\Delta^{2:6}$-*cyclo*hexadiene.

The ozonides of hydroaromatic compounds are much more stable than those derived from benzene compounds. Ring systems containing more than six carbon atoms yield ozonides, which are far less stable than those derived from hydroaromatic compounds. J. J. S.

Pseudo-acids. Arthur Hantzsch (*Ber.*, 1906, **39**, 2703—2705).—A reply to Euler (compare this vol., i, 576). C. S.

Constitution and Colour of Nitrophenols. Arthur Hantzsch (*Ber.*, 1906, **39**, 3072—3080. Compare this vol., i, 353).—Polemical. A reply to Kauffmann (this vol., i, 577). C. S.

Action of *tert.*-Alkyl Chlorides on *p*-Nitrophenol Salts. Leopold Spiegel and H. Kaufmann (*Ber.*, 1906, **39**, 2638—2640).—In studying the etherification of *p*-nitrophenol with various alcohols, Spiegel and Sabbath (Abstr., 1901, i, 533) attempted without success to prepare the *tert.*-butyl ether, decomposition taking place at higher temperatures, whilst at lower temperatures the silver salt of *p*-nitrophenol was converted into *p*-nitrophenol by the action of *tert.*-butyl chloride. The fact, however, that the silver salt in question contains water of crystallisation was overlooked at the time, so that action took place according to the equation $NO_2 \cdot C_6H_4 \cdot OAg + H_2O + CMe_3Cl = AgCl + NO_2 \cdot C_6H_4 \cdot OH + CMe_3 \cdot OH$.

The silver salt is unsuitable for the formation of the tertiary ether, since it does not become anhydrous when heated at 100°, and it decomposes explosively at 110°. The sodium salt, on the other hand, may be dehydrated completely at 120—130°, changing its tint from bright yellow to dark red in the process. When sodium *p*-nitrophenol, *tert.*-butyl chloride, and *tert.*-butyl alcohol are heated at 110° for six hours, sodium chloride and *p*-nitrophenol are obtained. At the same time *iso*butylene is formed by elimination of hydrogen chloride from the butyl chloride; it was identified by the formation of *αβ*-dibromo-*β*-methylpropane, $CMe_2Br \cdot CH_2Br$, by the action of bromine.

A. McK.

Solution Equilibrium between 2:4-Dinitrophenol and Aniline. Robert Kremann (*Monatsh.*, 1906, **27**, 627—630. Compare Abstr., 1905, ii, 77; Noelting and Sommerhoff, this vol., i, 157).—The melting-point curve for mixtures of 2:4-dinitrophenol and aniline drops from the melting point of the former and has a break representing a compound melting at 75°.

The influence of the two nitro-groups in the meta-position to each other is greater than that of the nitro- and hydroxy-groups in the ortho-position, as *o*-nitrophenols as such do not form compounds with aniline.

G. Y.

Selenium Compounds. F. Taboury (*Bull. Soc. chim.*, 1906, [iii], **35**, 668—674. Compare Abstr., 1903, i, 748).—Selenium reacts readily with magnesium alkyl haloids, and the complexes formed yield on treatment (1) with dilute acids, selenophenols and diselenides; (2) with acid chlorides or anhydrides, esters of the series of acids typified by $R \cdot CO \cdot SeH$; and (3) with alkyl iodides, mixed selenides. The compounds formed are strictly analogous with those obtained by the action of sulphur on magnesium alkyl haloids (Abstr., 1903, i, 748; 1904, i, 493; 1905, i, 56, 644).

Selenophenol boils at 182° (compare Krafft and Lyons, Abstr., 1894, i, 448). Phenyl diselenide melts at 62° (*loc. cit.*). *α-Selenonaphthol*, $C_{10}H_7 \cdot SeH$, is a slightly yellow liquid, boils at 165—167° under 20 mm. pressure, and evolves hydrogen selenide when heated at atmospheric pressure. *α-Naphthyl diselenide*, $C_{10}H_7 \cdot Se \cdot Se \cdot C_{10}H_7$, separates from alcohol in orange-yellow prisms and melts at 87—88°. *Benzyl α-naphthyl selenide* forms small, colourless prisms, melts at 68—69°, and yields a *picrate* which separates from ether in orange-red needles and melts at 118°. p-*Selenocresol*, $C_6H_4Me \cdot SeH$, crystallises from ether in colourless lamellæ, melts at 46—47°, and rapidly oxidises on exposure to air to p-*tolyl diselenide*,

$$C_6H_4Me \cdot Se \cdot Se \cdot C_6H_4Me,$$

which separates from alcohol in orange needles and melts at 47°. *Benzyl*-p-*tolyl selenide*, $CH_2Ph \cdot Se \cdot C_6H_4Me$, forms small, unctuous, colourless lamellæ and melts at 32—33°. p-*Tolyl selenobenzoate*,

$COPh\cdot Se\cdot C_6H_4Me$, crystallises in colourless prisms, melts at 71—72°, and reddens on exposure to light, due to the liberation of selenium. p-*Bromoselenophenol* separates from ether in colourless lamellæ, melts at about 75—77° and oxidises rapidly on exposure to air, forming p-*dibromobenzene diselenide*, $C_6H_4Br\cdot Se\cdot Se\cdot C_6H_4Br$, which forms yellow needles from alcohol and melts at 107—108°. p-*Chloroselenophenol* forms small, colourless lamellæ, melts at about 55°, and rapidly oxidises in air to p-*dichlorobenzene diselenide*, yellow needles, melting at 85—86°. p-*Methoxyphenyl selenobenzoate*, $COPh\cdot Se\cdot C_6H_4\cdot OMe$, forms colourless crystals from alcohol and melts at 97°. p-*Ethoxyselenophenol* is a colourless liquid, heavier than water, boils at 156—158° under 24 mm. pressure, and on oxidation of its solution in dilute potassium hydroxide yields p-*diethoxyphenyl diselenide*, $OEt\cdot C_6H_4\cdot Se\cdot Se\cdot C_6H_4\cdot OEt$, which crystallises in brilliant yellow lamellæ and melts at 65°. p-*Ethoxyphenyl selenobenzoate* separates from light petroleum in needles and melts at 94—95°. T. A. H.

Nitrophenolsulphonic Acids. ROBERT GNEHM and OSKAR KNECHT (*J. pr. Chem.*, 1906, [ii], **74**, 92—111. Compare this vol., i, 578; Franklin, Abstr., 1898, i, 522).—The action of sulphuryl chloride on *o*-nitroanisole leads to the formation of *p*-chloro-*o*-anisole, that of sulphuryl chloride and aluminium chloride to the formation of 4-chloro-2-nitrophenol and 4:6-dichloro-2-nitrophenol, and that of chlorosulphonic acid to the formation of o-*nitroanisole*-p-*sulphonic acid* together with a small amount of *p*-chloro-*o*-nitroanisole.

o-*Nitroanisole*-p-*sulphonic acid* crystallises from water in glistening, transparent plates, or from a mixture of ethyl acetate and benzene in white needles or large, glistening prisms. The *ammonium* and *barium* ($+7H_2O$) salts are described. o-*Nitroanisole*-p-*sulphonyl chloride*, $C_7H_6O_5NClS$, is prepared by the action of phosphorus pentachloride on ammonium *o*-nitroanisole-*p*-sulphonate on the water-bath, or by the action of nitric acid of sp. gr. 1·475 on anisole-*p*-sulphonyl chloride at −7° to −5°; it crystallises from a mixture of benzene and light petroleum in slender, white needles, melts at 66°, and is hydrolysed on prolonged boiling with water. o-*Nitroanisole*-p-*sulphonamide*, $C_7H_8O_5N_2S$, prepared by the action of ammonium carbonate on the sulphonyl chloride, crystallises in long, yellowish-white needles and melts at 146·3°.

Methyl o-*nitroanisole*-p-*sulphonate*, $C_8H_9O_6NS$, is obtained in only small amount by the action of an excess of methyl alcohol, whilst sodium *o*-nitroanisole-*p*-sulphonate is formed by the action of sodium methoxide in methyl-alcoholic solution on the sulphonyl chloride. The methyl ester is prepared in good yields by the action of sodium methoxide free from methyl alcohol, on the sulphonyl chloride in benzene solution; it crystallises in glistening, colourless prisms, melts at 83°, and is partially hydrolysed on recrystallisation from water, the unchanged ester separating in thin, white needles.

o-*Anisidine*-p-*sulphonic acid*, $C_7H_9O_4NS$, prepared by the reduction of *o*-nitroanisole-*p*-sulphonic acid by means of tin and hydrochloric acid, crystallises in glistening, thin needles, dissolves in water, becoming brown on oxidation by the air, gives a Bordeaux-red coloration with ferric chloride, reduces silver nitrate solutions, and forms readily soluble salts; nitrous acid or amyl nitrite converts it into the *diazo*-derivative, which couples with β-naphthol in alkaline solution, forming a bluish-red *azo-dye*. Complete reduction of *o*-nitroanisole-*p*-sulphonyl chloride by means of hydriodic acid, zinc dust and sulphuric acid, or tin and hydrochloric acid leads to the formation of m-*amino*-p-*methoxythiophenol*, which is isolated as the ***hydrochloride***, $C_7H_9ONS.HCl$; this crystallises in white, odourless needles, becomes brown at 170°, melts, forming a red liquid, at 230—235°, and is readily soluble in water or aqueous sodium hydroxide. The *mercuric* and *lead* salts are described. The free thiophenol forms stout, yellow, glistening crystals, is unstable, and is rapidly oxidised to the *disulphide hydrochloride*, $S_2[C_6H_3(OMe)\cdot NH_2]_2$, which forms white crystals and dissolves slowly in water. The *disulphide* separates from a mixture of toluene and light petroleum in spherical crystals, becomes violet on exposure to air, and gives with concentrated sulphuric acid a light green coloration changing through dark green to dark blue on warming. The action of nitrous acid on *m*-amino-*p*-methoxythiophenol leads to the formation of the *diazo*-derivative of the disulphide; this couples with β-naphthol in alkaline solution, forming a blood-red *azo-dye*, $S_2[C_6H_3(OMe)\cdot N_2\cdot C_{10}H_6\cdot OH]_2$.

In presence of sodium acetate, the thiophenol hydrochloride condenses with picryl chloride in boiling alcoholic solution, forming the *product*, $S_2[C_6H_3(OMe)\cdot NH\cdot C_6H_2(NO_2)_3]_2$, which crystallises in bluish-red, microscopic needles, and when heated melts, forming a red liquid, detonating at higher temperatures.

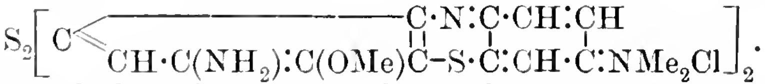
The *diacetyl* derivative of *m*-amino-*p*-methoxythiophenol,

$$C_{11}H_{13}O_3NS,$$

prepared by heating the hydrochloride with sodium acetate, zinc dust, and acetic anhydride, crystallises in glistening, transparent plates and melts at 85—86°.

Nitration of anisole-*p*-sulphonamide (compare Franklin, *loc. cit.*) leads to the formation of *m*-dinitrobenzene and a syrup which, on treatment with ammonia, yields *o*-nitroanisole-*p*-sulphonamide identical with the product obtained from *o*-nitroanisole.

The oxidation of a mixture of *m*-amino-*p*-methoxythiophenol hydrochloride and dimethyl-*p*-phenylenediaminethiosulphonic acid by means of potassium dichromate in dilute acetic acid solution at 0° leads to the formation of an *indaminethiosulphonic acid*, which forms a reddish-violet solution becoming blue and finally green as the oxidising agent is added, and when boiled with zinc chloride solution is converted into the *thiazine dye*,



$$S_2\left[C\begin{array}{l}\text{———————}C\cdot N{:}C\cdot CH{:}CH \\ CH\cdot C(NH_2){:}C(OMe)C{-}S\cdot C{:}CH\cdot C{:}NMe_2Cl\end{array}\right]_2.$$

This is obtained as a dark violet-blue powder with copper lustre, is slightly soluble in hot water, forming a violet-blue solution, gives red to blue flocculent precipitates with dilute hydrochloric or nitric acid, sodium carbonate or hydroxide, or ammonia, is decolorised by stannous chloride in hydrochloric acid solution, and with aqueous sodium sulphide forms a red, flocculent precipitate which is decolorised on heating. It dyes unmordanted cotton wool only feebly, more strongly in presence of sodium sulphide; cotton wool mordanted with tannin is dyed a pure blue, fast to washing. A table is given showing the results of the spectroscopic examination of the dye. The *acetyl* derivative of the leuco-compound is obtained as an impure yellowish-brown powder melting at 120—121°.

A *résumé* is given of the views of previous authors as to the constitution of the sulphur dyes. G. Y.

Aminophenolsulphonic and Aminocresolsulphonic Acids. GUSTAV SCHULTZ (*Ber.*, 1906, **39**, 3345—3347).—Aminophenolsulphonic acid III, formed by heating the anilinedisulphonic acid prepared from *m*-aminobenzenesulphonic acid with sodium hydroxide under pressure, is 3-aminophenol-4-sulphonic and not 3-aminophenol-6-sulphonic acid, whilst the anilinedisulphonic acid has the sulphonic groups in the positions 3 : 6 and not 3 : 4, as it readily yields benzene-*p*-disulphonic acid when converted into the corresponding hydrazine and boiled with aqueous cupric sulphate.

The *anilide*, $C_6H_4(SO_2{\cdot}NHPh)_2$, crystallises in nacreous leaflets and melts at 249°.

When diazotised and boiled with alcohol, 3-aminophenol-4-sulphonic acid yields an *ethoxyphenolsulphonic acid.* G. Y.

Preparation of a Di-*o*-anisidinedisulphonic Acid. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 172106).—Benzidine and tolidine on sulphonation furnish complex mixtures of mono- and di-sulphonic acids, sulphones, and sulphonesulphonic acids. It has now been discovered that di-*o*-anisidine, on the contrary, readily yields a homogeneous product consisting of a disulphonic acid when the reaction is effected at low temperatures.

The base is dissolved in four parts of fuming sulphuric acid (10 per cent. of SO_3) below 4°; subsequently the solution is heated slowly to 20—25° and then poured on to ice. The *di-o-anisidine-6 : 6′-disulphonic acid,* $C_{12}H_4(OMe)_2(NH_2)_2(SO_3H)_2$ [3 : 3′ : 4 : 4′ : 6 : 6′], which is somewhat soluble in water, is isolated in the form of its sparingly soluble normal *sodium* salt, this compound separating from its aqueous solution in silvery leaflets containing water of crystallisation. The acid itself is a white, crystalline substance, which may be employed in the production of colouring matters. G. T. M.

Ethers of Aminocresols and their Derivatives. LEOPOLD SPIEGEL, N. MUNBLIT, and H. KAUFMANN (*Ber.*, 1906, **39**, 3240—3251. Compare Abstr., 1901, i, 533).—2-*Methoxytolyl-3-carbamide,*

$$OMe{\cdot}C_6H_3Me{\cdot}NH{\cdot}CO{\cdot}NH_2,$$

obtained from 3-amino-2-methoxytoluene hydrochloride and carbamide on the water-bath, melts at 150°, and does not have a sweet taste. The corresponding *thiocarbamide,* $C_9H_{12}ON_2S$, melts at 137°.

3-*Amino-2-ethoxytoluene* is a yellow oil; the *hydrochloride,*

$$C_9H_{13}ON,HCl,$$

melts at 189°, the *carbamide* at 183°, the *thiocarbamide* at 140°.

3-*Nitro-2-propoxytoluene,* obtained from the potassium salt of the nitrocresol and propyl bromide in propyl alcohol at 160°, is a yellow oil, which boils at 210—212°. The *amino*-compound is a colourless liquid, the *hydrochloride* of which melts at 178°. The *carbamide*, $C_{11}H_{16}O_2N_2$, forms colourless needles and does not have a sweet taste; the *thiocarbamide* melts at 124°.

The *allyl ether* of 3-nitro-2-cresol is a yellow oil; the *amino*-compound is a red oil; the *hydrochloride* melts at 160°. The *carbamide*, obtained from the preceding salt and potassium cyanate, melts at 137°; the *thiocarbamide* at 130°.

The *benzyl ether* of 3-nitro-2-cresol is a red oil. The *amino*-compound, obtained by reduction with iron and 1 per cent. acetic acid solution, forms a *hydrochloride*, which melts at 178°. The *carbamide* melts at 113° and does not have a sweet taste.

2-*Ethoxytolyl*-5-*carbamide* melts at 158°.

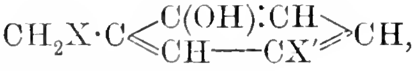
4-*Nitro*-2-*ethoxytoluene* melts at 61°, the *amino*-compound boils at 249—250°, and the *hydrochloride* melts at 245°. The *carbamide* melts at 161°; the *thiocarbamide* melts at 198° and has a bitter taste.

2-*Ethoxytolyl*-4-*hydrazine*, $OEt\cdot C_7H_6\cdot NH\cdot NH_2$, obtained by the reduction of the diazotised ethoxytoluidine hydrochloride, is an oil with the odour of phenylhydrazine. The *hydrochloride* melts and decomposes at 185—186°, and in aqueous solution yields, with dextrose and sodium acetate, 2-*ethoxytolyl*-4-d-*glucosazone*, $C_{24}H_{34}O_6N_4$, which forms microscopic, yellow crystals and melts at 168°.

Ethyl 2-*ethoxytolyl*-4-*carbamate*, $OEt\cdot C_7H_6\cdot NH\cdot CO_2Et$, obtained from an ethereal solution of ethyl chlorocarbonate and the ethoxytoluidine, melts at 68°.

The *ethylene ether* of 4-nitro-2-cresol, $C_2H_4(O\cdot C_7H_6\cdot NO_2)_2$, obtained from the potassium salt and ethylene dibromide, forms yellow needles and melts at 202°. The *amino*-compound, $C_{16}H_{20}O_2N_2$, melts at 129°; the *carbamide*, $C_{18}H_{22}O_4N_4$, melts at 218° and has a faint, bitter taste. C. S.

Constitution of Pseudo-phenols. KARL AUWERS (*Ber.*, 1906, 39, 3160—3181).—The author had suggested previously a phenolic structure for pseudo-phenols, whereas Zincke sometimes accepts the phenolic structure and sometimes the desmotropic ketonic structure. In the present paper, the author considers the question from the cryoscopic standpoint.

Pseudo-phenols of the type  $CH_2X\cdot C{<}\begin{matrix}C(OH){:}CH\\ CH{-\!-}CX'\end{matrix}{>}CH$, where X and X′ were negative substituents, were studied.

When 5-nitro-2-hydroxybenzyl chloride, melting at 128°, was boiled in acetic acid solution with sodium acetate, 5-*nitro*-2-*hydroxybenzyl acetate*, $OAc\cdot CH_2\cdot C_6H_3(NO_2)\cdot OH$, is formed; it separates from benzene in brown crystals and melts at 106·5—108·5°.

5-*Nitro*-2-*hydroxybenzyl bromide*, $CH_2Br\cdot C_6H_3(NO_2)\cdot OH$, prepared by passing a current of hydrogen bromide into a solution of either of the two preceding compounds at 70—80°, separates from benzene in leaflets and melts at 147°. By the action of bromine it forms 3-*bromo*-5-*nitrobenzyl bromide*, $NO_2\cdot C_6H_3Br\cdot CH_2Br$, which separates from glacial acetic acid in needles and melts at 155°. The 6-*bromo*-derivative of 5-*nitro*-o-*cresol*, $C_7H_6O_3NBr$, prepared in a similar manner, separates from glacial acetic acid in needles and melts at 118·5—119·5°.

Ethyl ω-*chloro*-6-*hydroxy*-m-*toluate*, $CH_2Cl\cdot C_6H_3(CH_2Cl)\cdot CO_2Et$, separates from benzene in needles and melts at 119·5°. Its *bromo*-derivative separates from glacial acetic acid in needles and melts at 142—143°.

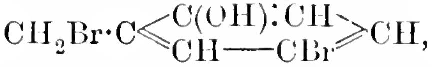
Ethyl 6-*hydroxy*-m-*toluate*, $OH\cdot C_6H_3Me\cdot CO_2Et$, prepared by oxidising the corresponding hydroxy-aldehyde by fusion with potash and then esterifying the acid formed, separates from a mixture of benzene and light petroleum in pink needles and melts at 98—99°.

3-Nitro-4-hydroxybenzyl chloride, $CH_2Cl\cdot C_6H_3(NO_2)\cdot OH$, melts at 75°, whereas the corresponding bromide, $C_7H_6O_3NBr$, obtained by passing a current of hydrogen bromide into a warm solution of the corresponding alcohol in acetic acid, melts at 83—85° and separates from glacial acetic acid in yellow needles.

Details of the cryoscopic determinations, which were conducted partly in benzene and partly in *p*-dibromobenzene solutions, are appended.

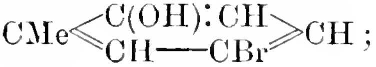
m-Bromo-*o*-hydroxybenzyl bromide behaves towards phenylcarbimide as a hydroxylic substance to form the *urethane*, $C_{14}H_{11}O_2NBr_2$, which crystallises in silky needles and melts at 170—171°.

A comparison of the pseudo-phenols and their parent true phenols with regard to cryoscopic behaviour indicates that the pseudo-phenols are phenolic in structure. The pseudo-phenol,



$$CH_2Br\cdot C{<}\begin{matrix}C(OH){:}CH\\ CH{-\!-}CBr\end{matrix}{>}CH,$$

was, for example, contrasted with the true phenol,

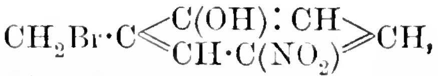


$$CMe{<}\begin{matrix}C(OH){:}CH\\ CH{-\!-}CBr\end{matrix}{>}CH;$$

the pseudo-phenols,

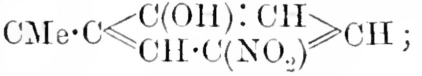
$$CH_2Cl\cdot C{<}\begin{matrix}C(OH){:}\,CH\\ CH\cdot C(NO_2)\end{matrix}{>}CH$$

and



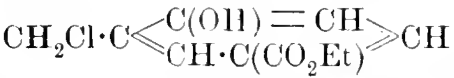
$$CH_2Br\cdot C{<}\begin{matrix}C(OH){:}\,CH\\ CH\cdot C(NO_2)\end{matrix}{>}CH,$$

with the true phenol,



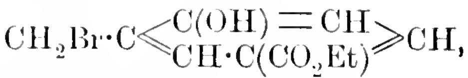
$$CMe\cdot C{<}\begin{matrix}C(OH){:}\,CH\\ CH\cdot C(NO_2)\end{matrix}{>}CH;$$

and the pseudo-phenols,



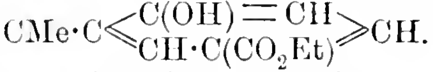
$$CH_2Cl\cdot C{<}\begin{matrix}C(OH){=}CH\\ CH\cdot C(CO_2Et)\end{matrix}{>}CH$$

and



$$CH_2Br\cdot C{<}\begin{matrix}C(OH){=}CH\\ CH\cdot C(CO_2Et)\end{matrix}{>}CH,$$

with the true phenol,



$$CMe\cdot C{<}\begin{matrix}C(OH){=}CH\\ CH\cdot C(CO_2Et)\end{matrix}{>}CH.$$

The author discusses at length the constitution of pseudo-phenols, and criticises in particular the views of Zincke. A. McK.

8-Amino-1-naphthol. Fritz Fichter and Rudolf Gageur (*Ber.*, 1906, **39**, 3331—3339. Compare Friedländer and Silberstern, Abstr., 1902, i, 793).—8-Acetylamino-1-naphthol, prepared by treating 8-amino-1-naphthol with finely-powdered sodium acetate, acetic anhydride, and glacial acetic acid, crystallises in colourless, broad needles or plates, melts at 168—169° (138°: Friedländer and Silberstern, *loc. cit.*), and boils at 170—172° under 16 mm. pressure. It reacts with nitrous acid, forming a *nitroso*-derivative, $C_{12}H_{10}O_3N_2$, which crystallises in brownish-red needles and decomposes at 175—180°. The *benzoyl* derivative, $NHBz\cdot C_{10}H_6\cdot OH$, crystallises in slender, colourless needles and melts at 193—194°. The *formyl* derivative, $COH\cdot NH\cdot C_{10}H_6\cdot OH$, crystallises in reddish-white needles and decomposes at 140—150°.

4-*Benzeneazo*-8-*acetylamino*-1-*naphthol*, $NPh{:}N\cdot C_{10}H_5(NHAc)\cdot OH$, formed by the action of diazobenzene chloride on 8-acetylamino-1-naphthol in alcoholic solution, crystallises in dark red, glistening needles, melts at 215—216°, and on reduction with stannous chloride and hydrochloric acid yields 4 : 8-diamino-1-naphthol. This forms a *diacetyl* derivative, $C_{14}H_{14}O_3N_2,H_2O$, crystallising in white needles and melting at 247°, and a *triacetyl* derivative, $OAc\cdot C_{10}H_5(NHAc)_2$, crystallising in stellate groups of small, white needles and melting at 258°.

The action of bromine on 8-acetylamino-1-naphthol in hot glacial acetic acid solution leads to the formation of *tribromo*-2-*methylnaphth*-peri-*oxazole dibromide*, $C_{10}H_3Br_3{<}\genfrac{}{}{0pt}{}{O}{N}{\gg}CMe,Br_2$, which crystallises from benzene in shining, yellow, matted, slender needles, melts at 235°, is stable towards alkali hydroxides and acids, and, when reduced with stannous chloride and hydrochloric acid in boiling glacial acetic acid solution, yields *tribromo-2-methylnaphth*-peri-*oxazole*, $C_{11}H_3OBr_3Me$; this crystallises in colourless needles, melts at 215°, is insoluble in aqueous alkali hydroxides, and forms the yellow dibromide when treated with bromine in glacial acetic acid solution.

Tribromo-2-phenylnaphth-peri-*oxazole*, $C_{10}H_3Br_3{<}\genfrac{}{}{0pt}{}{N}{O}{\gg}CPh$, prepared by the action of bromine on 8-benzoylamino-1-naphthol in hot glacial acetic acid solution, crystallises in slender, glistening needles, melts at 234°, and is highly stable.

8-*Acetylamino*-1-*naphthyl acetate*, $NHAc\cdot C_{10}H_6\cdot OAc$, formed by boiling 8-amino-1-naphthol hydrochloride with sodium acetate and acetic anhydride, crystallises in white needles, melts at 118·5°, decomposes slightly when distilled under reduced pressure, and when boiled with dilute sodium hydroxide yields 8-acetylamino-1-naphthol. With bromine in glacial acetic acid solution at the ordinary temperature, it forms a *monobromo*-derivative, $C_{14}H_{12}O_3NBr$, melting at 203°, but when boiled with an excess of bromine in glacial acetic acid solution yields tribromo-2-methylnaphth-*peri*-oxazole dibromide.

8-*Benzoylamino*-1-*naphthyl benzoate*, $C_{24}H_{17}O_3N$, formed by heating 8-amino-1-naphthol hydrochloride with sodium acetate and an excess of benzoic anhydride, crystallises in large, white needles and melts at 206—207°.

5-*Nitro*-8-*acetylamino*-1-*naphthyl acetate*, $NO_2\cdot C_{10}H_5(NHAc)\cdot OAc$, prepared by adding 8-acetylamino-1-naphthyl acetate to an excess of ice-cooled nitric acid of sp. gr. 1·38, crystallises from alcohol in long, light yellow, glistening needles, melts at 224°, and is hydrolysed by boiling dilute sodium hydroxide, yielding 5-*nitro*-8-*acetylamino*-1-*naphthol*, $NO_2\cdot C_{10}H_5(NHAc)\cdot OH$; this crystallises in red needles, melts at 192°, and dissolves in dilute alkali hydroxides, forming a red solution. It couples with diazonium salts in alkaline solution and on reduction with stannous chloride and hydrochloride yields an easily oxidisable diamino-1-naphthol.

8-*Acetylamino*-1 *methoxynaphthalene*, $NHAc{\cdot}C_{10}H_6{\cdot}OMe$, prepared by the action of methyl sulphate on 8-acetylamino-1-naphthol, crystallises in silvery-white needles, melts at 128°, boils at 138—140° under 14 mm. pressure, and forms a *monobromo*-derivative, $C_{13}H_{12}O_2NBr$, melting at 124°. When boiled with dilute hydrochloric acid, the acetylamino-methyl ether yields the *hydrochloride* of 8-amino-1-methoxynaphthalene, $C_{11}H_{11}ON,HCl$, which crystallises from alcohol; the *picrate*, $C_{11}H_{11}ON,C_6H_3O_7N_3$, crystallises in greenish-yellow needles and melts at 172°. The free *base*, $NH_2{\cdot}C_{10}H_6{\cdot}OMe$, is an oil which boils at 180—185° under 14 mm. pressure, and rapidly darkens. When diazotised and coupled with β-naphthol in sodium carbonate solution, it forms an *azo*-compound, $C_{21}H_{16}O_2N_2$, which crystallises from benzene in dark violet-red, metallic, hexagonal plates and melts at 177°. When boiled in sulphuric acid solution, the diazonium salt obtained from 8-amino-1-methoxynaphthalene yields the *monomethyl ether* of 1:8-dihydroxynaphthalene; the *picrate*, $C_{11}H_{10}O_2,C_6H_3O_7N_3$, melts at 173°.

When diazotised in well-cooled dilute solution and boiled with dilute sulphuric acid, 8-amino-1-naphthol yields α-naphthol. The action of nitrous acid on 8-amino-1-naphthol in concentrated solution leads to the formation of 2-*nitroso*-8-*amino*-1-*naphthol hydrochloride*, $OH{\cdot}C_{10}H_5(NO){\cdot}NH_2,HCl$, which crystallises in green needles, melts at 250°, and forms a violet coloration with aqueous sodium hydroxide. The concentrated strongly acid solution of the diazonium salt formed together with the nitroso-derivative is reduced by stannous chloride and hydrochloric acid to 2:8-*diamino*-1-*naphthol hydrochloride*; this crystallises in white needles and forms a *benzylidene* derivative, $CHPh{:}N{\cdot}C_{10}H_5(NH_2){\cdot}OH$, which separates from alcohol in yellow needles. The *triacetyl* derivative, $C_{16}H_{16}O_4N_2$, forms white, slender needles and melts at 234°. G. Y.

Reduction of Aromatic Sulpho-acids to Mercaptans by Alkali Hydrosulphides. Carl Schwalbe (*Ber.*, 1906, **39**, 3102—3105).—Sodium naphthalene-β-sulphonate and a 50 per cent. solution of potassium hydrosulphide are heated for three hours at 200—220° under a pressure of 10—12 atm. in an iron vessel. The precipitate obtained by heating the product with dilute hydrochloric acid is treated with ether, whereby β-naphthol and the mercaptan are extracted, whilst the disulphide remains undissolved and can be converted into the mercaptan by heating with potassium hydrosulphide and alcohol. The mercaptan yields dyes with diazo-compounds.

Benzene-sulphonic acid and -*m*-disulphonic acid yield coloured products, from which liquids can be obtained having the odour of mercaptans.

Primuline and thioflavin yield dyes containing sulphur. C. S.

Distribution of Auxochromes in the Molecule. Hugo Kauffmann and W. Franck (*Ber.*, 1906, **39**, 2722—2726).—The production of colour in a compound containing two or more auxochromes depends not so much on the relative positions of the auxochrome and chromophore as on the relative positions of the auxochromes themselves. The effect appears to be most pronounced when the two auxochromes are in the para-position, as, for example, in nitroquinol dimethyl ether; the effect is less when they are in the ortho-position, and is practically nil when in the meta-position; thus the ethers of 2- and of 4-nitroresorcinol are nearly colourless. The position of the chromophore is also of influence, since 4-nitroveratrole

$$[(OMe)_2 : NO_2 = 1 : 2 : 4]$$

is pale yellow, and the isomeric 3-nitro-compound, colourless. The effect of the positions of the auxochromes is seen by a comparison of 3-nitroveratrole and nitroquinol dimethyl ether.

2-Nitroresorcinol dimethyl ether, obtained by the action of methyl sulphate on 2-nitroresorcinol in the presence of sodium hydrogen carbonate, crystallises from acetic acid in colourless needles, melting at 129—130°.

4-*Nitroresorcinol diethyl ether* melts at 85°, and the isomeric 2-*nitro*-compound at 106—107°. J. J. S.

3 : 4-Diaminoguaiacol. FRITZ FICHTER and JULIUS SCHWAB (*Ber.*, 1906, **39**, 3339—3341. Compare Rupe, Abstr., 1898, i, 72).—4-*Acetylaminoguaiacyl acetate*, $C_{11}H_{13}O_4N$, prepared from 4-aminoguaiacol, crystallises from water in silvery scales, melts at 149°, and when boiled with aqueous sodium carbonate yields 4-*acetylaminoguaiacol*, $C_9H_{11}O_3N$, melting at 118°.

3-*Nitro*-4-*acetylaminoguaiacyl acetate*, $C_{11}H_{12}O_6N_2$, prepared by the action of ice-cooled concentrated nitric acid on 4-acetylaminoguaiacyl acetate, crystallises from water or alcohol in yellow, rhombic plates or needles, melts at 158°, and on hydrolysis yields 3-*nitro*-4-*acetylaminoguaiacol*, $C_8H_{10}O_5N_2$, crystallising in orange-red prisms and melting at 223°, together with 3-*nitro*-4-*aminoguaiacol*,

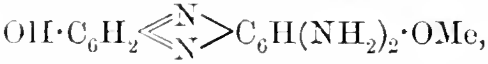
$$NH_2\cdot C_6H_2(NO_2)(OMe)\cdot OH,$$

crystallising from benzene or water in light red needles and melting at 169—171°.

3-*Nitro*-4-*benzoylaminoguaiacyl benzoate*, $C_{21}H_{16}O_6N_2$, crystallises in yellow, glistening needles and melts at 177°.

Reduction of 3-nitro-4-acetylaminoguaiacyl acetate with stannous chloride and hydrochloric acid leads to the formation of the *hydrochloride* of 3 : 4-diaminoguaiacol, which is readily oxidised, and condenses with benzil in alcoholic solution in presence of sodium acetate, forming 7-*hydroxy*-8-*methoxy*-2 : 3-*diphenylquinoxaline*, $C_{21}H_{16}O_2N_2$, crystallising in brownish-red, metallic needles and melting at 235°.

2 : 3-*Diamino*-8-*hydroxy*-1 : 9-*dimethoxyphenazine*,



$$OH\cdot C_6H_2<\overset{N}{\underset{N}{}}>C_6H(NH_2)_2\cdot OMe,$$

is formed by passing a current of air through an aqueous solution of 3 : 4-diaminoguaiacol hydrochloride in presence of ammonia; it crystallises in glistening scales or almost black, glistening needles, gives with concentrated sulphuric acid a green coloration, becoming blue, violet, and finally red on dilution, dissolves in alcohol, forming a brown solution with green fluorescence, and dyes animal and vegetable fibres a brownish-red. G. Y.

Constitution of Guaiacolmonosulphonic Acids and of a Mononitroguaiacol. LUDWIG PAUL (*Ber.*, 1906, **39**, 2773—2782).—*Potassium veratrolesulphonate* crystallises in colourless needles with $1\frac{1}{2}H_2O$ and melts and decomposes at about 300°; identical preparations are obtained either by sulphonating veratrole or by methylating Heyden's *o*- or *p*-guaiacolsulphonic acids (D.R.-P. 13820). *Veratrolesulphonic chloride* crystallises from ether in needles melting at 76°; the *amide* forms colourless needles melting at 136°. 5-*Nitroguaiacol*, prepared either by the action of fuming nitric acid on acetylguaiacol or by diazotising Cahours' (*Annalen*, 1850, **74**, 301) 4-nitro-*o*-anisidine, crystallises in needles and melts at 104°. Its constitution is confirmed by the conversion into Wisinger's β-nitrocatechol methyl ethyl ether (Abstr., 1902, i, 205), and the reduction of this to 4-methoxy-3-ethoxybenzenesulphonic acid, identified by means of its chloride and amides; the latter compound was also obtained from Heyden's *o*-guaiacolsulphonic acid, his *p*-guaiacolsulphonic acid yielding 3-methoxy-4-ethoxybenzenesulphonic acid, of which the *chloride* crystallises in yellow needles and melts at 72°, and the *amide* forms white needles melting at 192°.

E. F. A.

Behaviour of Cholesterol to Light. II. ERNST SCHULZE and ERNST WINTERSTEIN (*Zeit. physiol. Chem.*, 1906, **48**, 546—548. Compare Abstr., 1905, i, 128).—The changes previously described as occurring in cholesterol as the result of the action of light take place similarly in *iso*cholesterol from sheep's wool-fat, in phytosterol from wheat grains, and in ergosterol from the fungus *Boletus edulis.* The changes do not occur in sealed tubes in which the air has been displaced by carbon dioxide, and are therefore probably due to oxidation taking place on exposure to sunlight. W. D. H.

Arnidiol Phenylurethane. TIMOTHÉE KLOBB (*Bull. Soc. chim.*, 1906, [iii], **35**, 741—744. Compare Abstr., 1905, i, 594, and Bloch, Abstr., 1904, i, 236).—When heated at 150—180° with ammonia solution in a closed tube, the phenylurethane yields arnidiol, aniline, and carbon dioxide, and when heated alone at 250—300° for two hours in a closed tube it furnishes aniline, carbon dioxide, and a hydrocarbon, *arnidiene*, $C_{28}H_{42}$. The latter crystallises from ether in needles, melts at 234—236°, and then sublimes. It gives colour reactions similar to those of arnidiol. T. A. H.

Preparation of Aminoalkyl Esters. J. D. RIEDEL (D.R.-P. 169787. Compare this vol., i, 631).—The aminoalkyl esters having the general formula $NRR'\cdot CH_2\cdot CR''R'''\cdot O\cdot X$, where R, R', R'', and R''' are aryl or alkyl groups and X is an acyl group, are of great importance therapeutically, because they have the property of producing local anæsthesia without being poisonous; this physiological action seems to depend on the presence in the molecule of a secondary or tertiary amino-group and a tertiary alcohol group, which has been esterified with some suitable aromatic acid.

Dimethylaminotrimethylcarbinyl benzoate hydrochloride,

$$OBz\cdot CMe_2\cdot CH_2\cdot N(CH_3)_2,HCl,$$

results from the interaction of dimethylaminotrimethylcarbinol and benzoyl chloride in benzene solution; it crystallises from alcohol in transparent cubes, soluble in water and melting at 202°.

Phenyl dimethylaminodimethylcarbinyl benzoate hydrochloride,

$$OBz\cdot CMePh\cdot CH_2\cdot N(CH_3)_2,HCl,$$

obtained from phenyldimethylaminodimethylcarbinol by the Schotten Baumann reaction, crystallises from alcohol in plates, melts at 206°, and is readily soluble in water.

Dimethylaminodimethylethylcarbinyl benzoate, an oil boiling at 149° under 25 mm. pressure, yields a *hydrochloride* crystallising in needles or leaflets and melting at 175° and an *oxalate* which separates in fine needles and melts at 145°.

Dimethylaminodimethylpropylcarbinyl benzoate hydrochloride,

$$OBz\cdot CMePr^{\alpha}\cdot CH_2\cdot NMe_2,$$

crystallises from alcohol or ether in small, hygroscopic needles melting at 146°.

*Dimethylaminodimethyl*iso*amylcarbinyl benzoate hydrochloride,*

$$OBz\cdot CMe(CH_2\cdot CH_2\cdot CHMe_2)\cdot CH_2\cdot NMe_2,HCl,$$

crystallises from ether-alcohol in silky needles melting at 138°; it is very soluble in water and insoluble in boiling acetone; its taste is bitter and acrid. The platinichloride melts at 178°.

The *hydrochlorides* of *dimethylaminomethyldiethylcarbinyl* and *benzyldimethylaminodimethylcarbinyl benzoates* are well-defined crystalline salts melting respectively at 189° and 195°.

Dimethylaminotrimethylcarbinyl cinnamate hydrochloride,

$$CHPh\cdot CH\!:\!CH\cdot CO\cdot O\cdot CMe_2\cdot CH_2\cdot NMe_2,HCl,$$

prepared by the interaction of dimethylaminotrimethylcarbinol and cinnamyl chloride in benzene solution, separates in large, tabular crystals which dissolve in acetone and are moderately soluble in hot alcohol, but much less soluble in the cold solvent; it melts at 208°.

The cinnamyl derivatives of the other aminoalcohols were similarly prepared, and all yielded well-defined crystalline hydrochlorides with definite melting points.

Dimethylaminotrimethylcarbinyl iso*valerate hydrochloride,*

$$CHMe_2\cdot CH_2\cdot CO\cdot O\cdot CMe_2\cdot CH_2\cdot NMe_2,HCl,$$

obtained by employing *iso*valeryl chloride instead of cinnamyl chloride in the preceding preparation, separates in large leaflets which are greasy to the touch and have a bitter taste; it is readily soluble in the ordinary solvents except cold ether and petroleum; it melts indefinitely at 112°.

Dimethylaminodimethylethylcarbinyl diethylcarbamate hydrochloride, $NEt_2\cdot CO\cdot O\cdot CMeEt\cdot CH_2\cdot NMe_2,HCl$, was prepared by heating for one day on the water-bath equivalent quantities of dimethylaminodimethylethylcarbinol and diethylcarbamyl chloride, $NEt_2\cdot COCl$; when recrystallised from ether alcohol it separates in lustrous needles or leaflets and decomposes at 144°.

Dimethylaminodimethylethylcarbinyl acetate,

$$CMeO\cdot O\cdot CMeEt,CH_2\cdot NMe_2,$$

was produced by heating the corresponding carbinol with acetic anhydride for four hours at 120°; it boils at 80—85° under 32 mm. pressure and rapidly darkens and decomposes on exposure to light.

G. T. M.

Preparation of the Alkali Salts of Organic Acids from the Corresponding Nitriles and Amides. DEUTSCHE GOLD- UND SILBER-SCHEIDE-ANSTALT VORM. RÖSSLER (D.R.-P. 169186).—The organic nitriles or amides are hydrolysed by a mixture of equivalent quantities of calcium hydroxide and some alkali salt, such as the carbonate or oxalate, which is capable of forming a sparingly soluble calcium salt, the alkali salt of the organic acid being subsequently obtained by evaporating the filtrate. The process is applicable in the following cases: phenylaminoacetonitrile, acetonitrile, benzonitrile, acetamide, and benzamide. G. T. M.

Alkylation and Arylation of Anthranilic Acid. JOSEF HOUBEN and WALTER BRASSERT (*Ber.*, 1906, **39**, 3233—3240).—Willstätter and Kahn's method (Abstr., 1904, i, 235) for alkylating anthranilic acid was modified by conducting the alkylation with methyl sulphate in glacial acetic acid solution. When a mixture of anthranilic acid, sodium carbonate, water, and methyl sulphate is boiled, methyl methylanthranilate is formed in addition to methylanthranilic acid.

Whilst a mixture of methylanthranilic acid, dimethylanthranilic acid, and methyl anthranilate is produced by boiling together anthranilic acid, methyl iodide, and aqueous potassium hydroxide according to H. Meyer's method, it is possible to obtain methylanthranilic acid in good yield if an excess of alkali is avoided.

Anthranilic acid may also be methylated by boiling it with methyl sulphate and water. Although in the special case of anthranilic acid the yield of the methylated acid is not as good as that from other methods, the results with *m*- and *p*-aminobenzoic acids are good, and the method is recommended for the methylation of substances which are sensitive towards alkalis.

Anthranilic acid may be ethylated either by H. Meyer's method or by ethyl sulphate. Ethyl bromide is a convenient substitute for ethyl iodide when Meyer's method is used.

Benzylanthranilic acid was obtained by boiling together anthranilic acid, water, potassium carbonate, and benzyl chloride. *p*-Nitrobenzylanthranilic acid may be prepared in a similar manner.

Phenylanthranilic acid was obtained by heating a mixture of anthranilic acid, copper, bromobenzene, sodium carbonate, and water (compare Goldberg, this vol., i, 426).

α-Naphthylanthranilic acid was obtained by heating a mixture of anthranilic acid, sodium carbonate, water, copper, and α-naphthyl bromide.

Allyl chloride differs from propyl and *iso*butyl chlorides by reacting readily with anthranilic acid and aqueous potassium carbonate to form allylanthranilic acid. A. McK.

Preparation of the Alkamine Esters of *o*- and *m*-Aminobenzoic Acids. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 170587, 172301).—The *o-nitrobenzoyl* ester of diethylaminoethanol is an oil produced by condensing *o*-nitrobenzoyl chloride and diethylaminoethanol in benzene solutions; on reduction it yields an oily o-*aminobenzoyl* ester, the *monohydrochloride* of which separates from alcohol in colourless crystals and melts at 125—127°.

The *m*-compound can be prepared either in the preceding manner or as follows. Methyl *m*-aminobenzoate was heated for twelve hours with diethylaminoethanol and the excess of the latter removed by distillation under reduced pressure; the product was rendered neutral with hydrochloric acid, in which it dissolved. The solution, after extraction with ether to remove the unaltered methyl *m*-aminobenzoate, was concentrated to obtain m-*aminobenzoyldiethylaminoethanol hydrochloride,* which, when recrystallised from alcohol, separated in colourless prisms melting at 118—120°. The base set free by alkalis solidifies on cooling, and after crystallisation from light petroleum melts at 45—47°.

m-*Aminobenzoyl-α-hydroxyethylpiperidine* was prepared either by heating ethyl *m*-aminobenzoate and α-hydroxyethylpiperidine or by mixing α-hydroxyethylpiperidine and *m*-aminobenzoic acid with cold concentrated sulphuric acid and then warming the mixture on the water-bath. In both cases the base was purified by means of its monohydrochloride, then set free by alkalis and recrystallised from light petroleum, when it melted at 73—74°.

Chloroethyl m-*aminobenzoate,* obtained either by esterifying *m*-aminobenzoic acid with ethylene chlorohydrin, or by reducing *m*-nitrobenzoyl ethylene chlorohydrin, was heated with diethylamine at 100—120°. The oily m-*aminobenzoate* of diethylaminoethanol solidified on cooling and was purified by conversion into its monohydrochloride, which crystallised from alcohol in colourless prisms and melted at 118—120°.

The hitherto unknown alkamine esters of the *o*- and *m*-azobenzoic acids are prepared by heating the alkyl azobenzoates with the alkamines; the oily or crystalline products, which are red when reduced with stannous chloride or tin and hydrochloric acid, yield the corresponding alkamine esters of the aminobenzoic acids. Thus *m*-azobenzoylpiperidoethanol, which separates in orange-red crystals melting at 72—74°, furnishes m-*aminobenzoylpiperidoethanol,* melting at 79—80° and yielding a hydrochloride melting at 187—189°.

o-*Aminobenzoyldiethylaminoethanol* is prepared similarly; it is oily and forms a crystalline hydrochloride melting at 125—126°

m-*Aminobenzoyldiethylaminoethanol* melts at 45—47°; and its hydrochloride at 118—120°. G. T. M.

Preparation of *N*-Alkylated Alkamine Esters of *o*- and *m*-Aminobenzoic Acids. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 172447. Compare preceding abstract).—*N*-Dimethylanthranilic acid and diethylaminoethanol when condensed in concentrated sulphuric acid, first at 0° and then on the water-bath, give rise to an oily *alkamine* ester, the hydrochloride of which melts at 135—137°.

N-Ethylanthranilic acid and hydroxyethylpiperidine, when similarly condensed, yield an oily alkamine ester, the hydrated hydrochloride of which melts at 106—108°, whilst the dehydrated substance melts at 142—145°.

The *alkamine* ester, from *m*-dimethylaminobenzoic acid and diethyl-

aminoethanol, is an oil, giving rise to a crystalline hydrochloride melting at 187°.
G. T. M.

Preparation of the Alkamine Esters of *p*-Aminobenzoic Acid. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 172568).—The alkamine esters of *p*-aminobenzoic acid may be prepared by heating the alkyl esters of this acid with an alkamine at the boiling point of the latter, the condensation being accompanied by the elimination of alcohol. The *p-aminobenzoate* of *hydroxyethylpiperidine* is obtained in the form of its crystalline *hydrochloride* by heating ethyl *p*-aminobenzoate with hydroxyethylpiperidine at 200—210° for four to six hours, distilling off the excess of alkamine under reduced pressure, neutralising the residue with dilute hydrochloric acid, filtering off unaltered ethyl *p*-aminobenzoate, and concentrating the filtrate. The alkamine ester itself was set free by alkalis as an oil which soon solidified; after crystallisation from light petroleum, the ester was obtained in colourless needles melting at 90°.

The *alkamine* ester from *p*-dimethylaminobenzoic acid and hydroxyethylpiperidine, when crystallised from light petroleum, melts at 38—40°. The corresponding ester from hydroxyethyldiethylamine melted at 59—60°. Both these esters form crystallisable hydrochlorides.

The esters may be employed in therapeutics as local anaesthetics.
G. T. M.

Carbithionic Acids. I. Arylcarbithionic Acids. JOSEF HOUBEN [with HEINRICH POHL] (*Ber.*, 1906, **39**, 3219—3233. Compare Houben and Kesselkaul, Abstr., 1903, i, 42).—*Phenylcarbithionic acid* (*dithiobenzoic acid*), $C_6H_5\cdot CS\cdot SH$, prepared by the action of magnesium phenyl bromide (1 mol.) on carbon disulphide (1 mol.), is a reddish-violet, pungent oil. Its ethereal solution is carmine-red. Its *lead* salt separates from toluene in purple leaflets or needles and melts at 204·5° (corr.). Its *zinc* salt is a yellow, amorphous solid and begins to decompose at about 100°. Its *mercury* salt separates from benzene in leaflets with a bronze lustre and melts at 150°.

Thiobenzoyl disulphide, $S_2(CSPh)_2$, prepared by the addition of a solution of iodine in potassium iodide to sodium dithiobenzoate, is a crystalline solid and melts at 92·5°.

Details are given for the preparation of *benzylcarbithionic acid* (*dithiophenylacetic acid*, $CH_2Ph\cdot CS_2H$ (compare Houben and Kesselkaul, *loc. cit.*). The *lead* salt separates from benzene in yellow needles and melts at 149°. The *zinc* salt crystallises from benzene in yellow leaflets and melts at 221°.

Thiophenylacetyl disulphide, $S_2(CS\cdot CH_2Ph)_2$, prepared by the action of a solution of iodine in potassium iodide on sodium dithiophenylacetate, melts at 78°.

a-Naphthylcarbithionic acid (*a-dithionaphthoic acid*), $C_{10}H_7\cdot CS\cdot SH$, prepared from magnesium *a*-naphthyl bromide and carbon disulphide, is a dark red oil. Its *lead* salt separates from benzene in needles; its *zinc* salt is a yellow solid; its iron salt, $(C_{10}H_7\cdot CS_2)_3Fe$, separates from ether in green leaflets.

a-Thionaphthoyl disulphide, $S_2(CS\cdot C_{10}H_7)_2$, prepared by the action of a solution of iodine in potassium iodide on sodium *a*-naphthylcarbithionate, melts at 169°. Its solution in concentrated sulphuric acid assumes a dark blue shade, which disappears on the addition of water. It is oxidised to *a*-naphthoic acid by concentrated nitric acid.

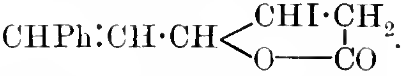
p-*Bromophenylcarbithionic* [p-*bromodithiobenzoic*] *acid*,

$$C_6H_4Br\cdot CS\cdot SH,$$

prepared by the action of magnesium *p*-dibromophenyl on carbon disulphide, is a brownish-red oil. Its *lead* salt may be crystallised from benzene or toluene; its *zinc* salt is a yellow, amorphous powder; its *iron* salt is a dark green powder. A. McK.

Action of Acetyl Bromide on Benzyl Cyanide. Franz Kunckell [with F. Flos] (*Ber.*, 1906, **39**, 3145—3146).—p-*Acetylbenzylcyanide* [p-*acetylphenylacetonitrile*], $C_6H_4Ac\cdot CH_2\cdot CN$, prepared by the addition of aluminium chloride to a mixture of phenylacetonitrile, acetyl bromide, and carbon disulphide, separates from a mixture of benzene and light petroleum in white needles, melts at 83—84°, and boils with slight decomposition at 333—334°. Its *hydrazone* melts at 112—114°. Its *oxime* separates from benzene in cubes and melts at 123°.

m-*Acetylphenylacetonitrile*, obtained as a by-product in the preceding reaction, is a yellow oil which boils at 327—331° and has the sp. gr. 1·109 at 23°. When oxidised by permanganate, it yields *iso*phthalic acid. A. McK.

Action of Nascent Hypoiodous Acid on Acids containing an Ethylenic Linking. Iodo-lactones. J. Bougault (*Compt. rend.*, 1906, **143**, 398—400. Compare Abstr., 1905, i, 9).—Acids of the type $CHR{:}CH\cdot CH{:}CH\cdot CO_2H$ (sorbic, piperic, or cinnamenylacrylic acid), although containing an ethylenic linking in the $\gamma\delta$-position, do not react with iodine and yellow mercuric oxide or iodine and alkali carbonates (nascent hypoiodous acid), but cinnamenyl*iso*crotonic acid (this vol., i, 671) yields the iodo-lactone,  $CHPh{:}CH\cdot CH\Big<\begin{array}{l}CHI\cdot CH_2\\ O\text{——}CO\end{array}$. *a*-Ketonic acids of the type $CHR{:}CH\cdot CO\cdot CO_2H$ (benzylidene-, piperylidene-, cinnamylidene-, or furfurylidene-pyruvic acid) do not form iodo-lactones by the action of nascent hypoiodous acid, but the corresponding *a*-hydroxy-acids, $CHR{:}CH\cdot CH(OH)\cdot CO_2H$, obtained by the reducing action of sodium amalgam, readily yield iodo-lactones. Neither β-benzylidenelævulic acid nor cinnamenylparaconic acid forms an iodo-lactone, although each contains an ethylenic linking in the $\beta\gamma$-position. M. A. W.

Syntheses and Properties of some New Phenanthrene Derivatives. Robert Pschorr (*Ber.*, 1906, **39**, 3106—3124. Compare Abstr., 1896, i, 303; 1900, i, 232, 233, 487, 488, 489; 1902, i, 96; 1903, i, 167).—[With H. Tappen.]—*a*-o-*Tolyl-2-nitro-3:4-dimethoxycinnamic acid*, $NO_2\cdot C_6H_2(OMe)_2\cdot CH{:}C(C_7H_7)\cdot CO_2H$, resulting from the condensation of sodium *o*-tolylacetate (compare Radziszewski and Wispek, Abstr., 1885, 889), *vic*-*o*-nitrovanillin methyl ether (Abstr., 1899, i, 178), and acetic anhydride at 100°, forms slender needles and melts at 255° (corr.). The corresponding *amino*-acid, obtained by reduction with ferrous sulphate and ammonium hydroxide, separates from alcohol in yellow prisms and melts at 192° (corr.). The *diazonium chloride*, $C_{18}H_{18}O_4N_2Cl$, precipitated from alcoholic solution by ether, forms yellow prisms and melts and decomposes at 101—102°.

3 : 4-*Dimethoxy-8-methylphenanthrene-9-carboxylic acid*, $C_{18}H_{16}O_4$, prepared by warming the diazonium chloride and aqueous sodium carbonate, melts at 178—180° (corr.), and by distillation under 160 mm. pressure yields 3 : 4-*dimethoxy-8-methylphenanthrene*, $C_{17}H_{16}O_2$, which melts at 68°.

[With R. HOFMANN.]—*a-o-Tolyl-2-nitrocinnamic acid*,

$$NO_2\cdot C_6H_4\cdot CH:C(C_7H_7)\cdot CO_2H,$$

obtained from *o*-nitrobenzaldehyde, acetic anhydride, and sodium *o*-tolylacetate at 100°, melts at 168° (corr.), and by reduction yields the *amino*-acid, $C_{16}H_{15}O_2N$, which occurs in two modifications. It separates from alcohol in yellow, hexagonal prisms which melt at 225° (corr.), whereas a colourless form is precipitated by acidifying the cold ammoniacal solution of the acid. The latter changes into the yellow modification at 170° or in contact with water free from acid.

8-*Methylphenanthrene-9-carboxylic acid*, $C_{16}H_{12}O_2$, is obtained when the diazotised acid in dilute sulphuric acid is treated with copper powder; it crystallises in flat needles, sinters at 177°, and melts at 181—182° (corr.). By distillation under 160 mm. pressure it yields 1-*methylphenanthrene*, $C_{15}H_{12}$, which melts at 123° (corr.) and forms a *picrate*, $C_{15}H_{12},C_6H_3O_7N_3$, melting at 139° (corr.).

1-Methylphenanthrene is quite stable to potassium permanganate, but by potassium dichromate and sulphuric acid is oxidised to 1-*methylphenanthraquinone*, $C_{15}H_{10}O_2$, which forms red leaflets and melts at 196° (corr.).

[With F. QUADE.]—*a-p-Tolyl-2-nitrocinnamic acid*, obtained in a similar manner to the preceding isomeride, melts at 204° (corr.). 5-*Nitro-8-methylstilbene*, $C_{15}H_{13}O_2N$, occurring as a by-product, forms red prisms and melts at 211° (corr.). The *amino* acid, $C_{16}H_{15}O_2N$, forms colourless needles, and melts at 206° (corr.). After diazotisation, treatment with copper powder in acid solution or warming with aqueous sodium carbonate produces 6-*methylphenanthrene-9-carboxylic acid* in 20 per cent. yield. A 70 per cent. yield is obtained by diazotising with amyl nitrite in alcoholic hydrogen chloride solution, diluting with water, and adding copper powder. The acid separates from glacial acetic acid in aggregates of light yellow needles, melts at 238° (corr.), and by distillation at the ordinary pressure yields 3-*methylphenanthrene*, which melts at 65°, crystallises in long prisms, forms a *dibromide* melting at 86—87°, and a *picrate* which melts at 141° (corr.).

a-p-Tolyl-2-nitro-3 : 4-dimethoxycinnamic acid, $C_{18}H_{17}O_6N$, melts at 245° (corr.); the corresponding *amino*-acid, $C_{18}H_{19}O_4N$, at 203° (corr.).

3 : 4-*Dimethoxy-6-methylphenanthrene-9-carboxylic acid*, $C_{18}H_{16}O_4$, forms hexagonal plates, melts at 253° (corr.), and by distillation in a vacuum yields 3 : 4-*dimethoxy-6-methylphenanthrene*, $C_{17}H_{16}O_2$, which

melts at 70—72°, forms a *dibromide*, $C_{17}H_{16}O_2Br_2$, melting at 126—127°, and a *picrate*, melting at 118—119°.

[With H. Tappen.]—α-o-*Carboxyphenyl-2-nitrocinnamic acid*,
$NO_2\cdot C_6H_4\cdot CH:C(C_6H_4\cdot CO_2H)\cdot CO_2H$,
obtained from sodium homophthalate, melts at 229° (corr.), and by reduction yields the *amino*-acid, $C_{16}H_{13}O_4N$, which forms slender needles and melts at 255—256° (corr.).

By warming the solution of the diazotised acid, a mixture of phenanthrene-8 : 9-dicarboxylic acid and its *anhydride* is obtained, which is converted wholly into the latter by crystallisation from glacial acetic acid. It forms glistening needles, melts at 283—284° (corr.), and with ammonia yields the *imide*, $C_{16}H_9O_2N$, which sublimes in elongated crystals and melts at 308—309° (corr.). The pure acid has not been obtained.

α-o-*Carboxyphenyl-2-nitro-3 : 4-dimethoxycinnamic acid*,
$NO_2\cdot C_6H_2(OMe)_2\cdot CH:C(C_6H_4\cdot CO_2H)\cdot CO_2H$,
forms yellow needles and melts and decomposes at 259—260° (corr.). The *anhydride*, $C_{18}H_{13}O_7N$, also obtained in the condensation, melts at 217° (corr.). The amino-acid is obtained readily, but not crystallised, owing to the formation of the anhydride. When the diazotised acid is warmed, 3 : 4 dimethoxyphenanthrene-8 : 9-dicarboxylic acid and its *anhydride*, $C_{18}H_{12}O_5$, are obtained. By crystallisation, from glacial acetic acid, the mixture is converted entirely into the anhydride, which forms yellow needles and melts at 283—284° (corr.).

[With M. Schütz.]—α-p-*Bromophenyl-2-nitrocinnamic acid*,
$NO_2\cdot C_6H_4\cdot CH:C(C_6H_4Br)\cdot CO_2H$,
obtained from sodium *p*-bromophenylacetate (the *amide* of which,
C_8H_8ONBr,
melts at 192—194°), crystallises in yellow needles, melts at 187°, and by reduction yields the *amino*-acid, $C_{15}H_{12}O_2NBr$, which occurs in yellow needles melting at 213°, or in colourless crystals melting at 222—223°. When the amino-acid is warmed with acetic anhydride and concentrated sulphuric acid, β-p-*bromophenylcarbostyril*,
$C_{15}H_{10}ONBr$,
is formed, which melts at 266—267°.

When the acid, dissolved in sodium hydroxide solution, and sodium nitrite, are added to cold dilute sulphuric acid, after some time the diazo-compound separates in yellow flocks. By warming the solution, 3-*bromophenanthrene-9-carboxylic acid*, $C_{15}H_9O_2Br$, is obtained, which forms yellow needles, melts at 290—291°, evolves hydrogen bromide on distillation, and is oxidised to 3-bromophenanthraquinone (compare Schmidt, Abstr., 1904, i, 1034) by chromic and acetic acids.

[With J. Popovici.]—α-o-*Bromophenyl-2-nitro-3 : 4-dimethoxycinnamic acid*, $NO_2\cdot C_6H_2(OMe)_2\cdot CH:C(C_6H_4Br)\cdot CO_2H$, melts at 266—267° (corr.). The *amino*-acid, $C_{17}H_{16}O_4NBr$, forms yellow prisms, melts at 218° (corr.), and after diazotisation with amyl nitrite yields 8-*bromo-3 : 4-dimethoxyphenanthrene-9-carboxylic acid*, $C_{17}H_{13}O_4Br$, which separates from hot alcohol in colourless prisms, melts at 228—229° (corr.), and by distillation in a vacuum loses carbon dioxide and hydrogen bromide, yielding a mixture of 8-*bromo-3 : 4-dimethoxyphenanthrene*, which melts at 81—82°, and the *lactone* of 8-hydroxy-

3 : 4-dimethoxyphenanthrene-9-carboxylic acid. The former, which is soluble in ether, is purified in the form of the *picrate*, which melts at 117°. The lactone, which is insoluble in ether, separates from alcohol in slender, yellow needles and melts at 160° (corr.). When its solution in sodium hydroxide is acidified, the *acid* $C_{17}H_{14}O_5$ is precipitated ; it crystallises in long needles and melts at 193° (corr.).

a-o-*Nitrophenyl-2-nitrocinnamic acid*,

$$NO_2 \cdot C_6H_4 \cdot CH \colon C(C_6H_4 \cdot NO_2) \cdot CO_2H,$$

melts at 207° (corr.). The diamino-acid has not been isolated ; by acidifying its ammoniacal solution, *a-*o-*aminophenyl-2-aminocinnamic anhydride* (3-o-*aminobenzylideneoxindole*), $C_{15}H_{12}ON_2$, is obtained, which forms yellow prisms and melts at 233—234° (corr.). By treating the diazonium compound with copper powder, the *anhydride* of 8-aminophenanthrene-9-carboxylic acid, $C_{15}H_9ON$, is obtained ; it separates from dilute alcohol in faintly yellow prisms and melts at 231° (corr.).

The condensation of *vic-o-*aminovanillin and sodium *o*-nitrophenylacetate leads to the formation of the *anhydride* of *a-o-*nitrophenyl-2-amino-4-acetoxy-3-methoxycinnamic acid (o-*nitro-4-acetoxy-3-methoxycarbostyril*), $C_{18}H_{14}O_6N_2$, which melts at 261° (corr.).

[With F. Quade.]—The condensation of 2-nitro-5-hydroxybenzaldehyde and sodium phenylacetate leads to the formation of *a-phenyl-2-nitro-5-hydroxycinnamic acid*,

$$NO_2 \cdot C_6H_3(OH) \cdot CH \colon CPh \cdot CO_2H,$$

which melts at 219—220°. The *amino*-acid, $C_{15}H_{13}O_3N$, forms yellowish-brown prisms and melts at 237—239° (corr.).

2-*Hydroxyphenanthrene-9-carboxylic acid*, $C_{15}H_{10}O_3$, melts at 278° (corr.), and the *acetyl* derivative, $C_{17}H_{12}O_4$, at 223° (corr.).

a-Phenyl-2-nitro-3-acetoxycinnamic acid, $C_{17}H_{13}O_6N$, results from the reaction between 2-nitro-3-hydroxybenzaldehyde, sodium phenylacetate, and acetic anhydride ; it forms yellow prisms, melts at 254° (corr.), and by reduction and simultaneous hydrolysis yields *a-phenyl-2-amino-3-hydroxycinnamic acid*, $C_{15}H_{13}O_3N$, which separates from dilute methyl alcohol in yellow, rhombic plates, melts at 201° (corr.), and does not form phenanthrene derivatives. C. S.

Electrolytic Reduction of Aromatic Carboxylic Acids. Carl Mettler (*Ber.*, 1906, **39**, 2933—2942. Compare Abstr., 1905, i, 436 ; this vol., i, 497).—The reductions were performed in an apparatus consisting of a porous cell, containing a lead anode and filled with dilute sulphuric acid, placed in a beaker containing a lead electrode and the cathode liquid, generally a solution of the acid to be reduced in 20—30 per cent. alcoholic sulphuric acid. A number of aromatic acids were thus reduced to the corresponding alcohols. 3 : 5-*Dichlorosaligenin*, obtained from 3 : 5-dichlorosalicylic acid, crystallised in needles melting at 82° ; 3 : 5-dibromosaligenin melts at 87—88°. The *ethyl ether* of 3 : 5-*dichloro*-p-*hydroxybenzyl alcohol* melts at 86°. *o*-Diphenyldicarboxylic acid is reduced to phenanthraquinone ; phthalic acid and terephthalic acid give the corresponding dihydro-derivatives.

E. F. A.

Preparation of Menthyl Salicylate. Bertrand Bibus and Rudolf Scheuble (D.R.-P. 171453. Compare Trans., 1903, **83**, 1213, and 1904, **85**, 1262).—The esterification of menthol is an operation which is effected only with some difficulty owing to the sensitiveness of this alcohol to the action of dehydrating agents, especially when employed at high temperatures. This difficulty is increased when the acid employed also tends to decompose at high temperatures. It has now been found that *menthyl salicylate* may be obtained in fairly good yield (75—80 per cent. of the calculated amount) by heating 30 parts of menthol and 140 parts of salicylic acid at 140—220° in a current of gas such as hydrogen or carbon dioxide. After removing the unchanged acid with aqueous alkali carbonate, the oily residue is fractionated. The ester is a viscid, colourless liquid, having a sweet taste and but very little odour; it is insoluble in water, but dissolves in the ordinary organic solvents. It can only be distilled under diminished pressure, when it boils at 190° and 175° under 15 and 10 mm. pressure respectively. G. T. M.

Preparation of Tyrosine from Silk. Emil Abderhalden and Yutaka Teruuchi (*Zeit. physiol. Chem.*, 1906, **48**, 528—529).—The usual method of preparing tyrosine from proteids, by hydrolysing with boiling 25 per cent. sulphuric acid and removal of the acid with baryta, is tedious, and leads to loss of tyrosine by its inclusion in the precipitate of barium sulphate. The preparation is simplified by the use of fuming hydrochloric acid, evaporating to dryness, and taking up the residue with water. This is again evaporated to dryness and the procedure repeated. After boiling with animal charcoal, the remaining acid is neutralised exactly with sodium hydroxide, when the tyrosine falls out of solution in an almost pure condition. One recrystallisation renders it quite pure. One kilo. of silk yielded 50—65 grams of tyrosine. Cystine may be obtained in a very similar way. W. D. H.

o-, *m*-, and *p*-**Iodohippuric Acids.** Treat B. Johnson and Harold A. Meade (*Amer. Chem. J.*, 1906, **36**, 294—301).—o-*Iodohippuric acid*, $C_6H_4I\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$, obtained by the action of *o*-iodobenzoyl chloride on aminoacetic acid in presence of sodium hydroxide, crystallises from hot water in clusters of radiating needles and melts at 167°. The *nitrile* separates from alcohol in prisms and melts at 158°. The *ethyl* ester forms irregular prisms and melts at 79—80°.

m-Iodohippuric acid, prepared by warming an aqueous solution of potassium iodide and *m*-diazohippuric acid, crystallises from hot water in thin plates, melts at 155—156°, and is probably identical with the acid obtained by Griess (Abstr., 1871, 702) by the action of hydriodic acid on diazohippuric acid.

p-*Iodohippuric acid*, obtained by treating aminoacetic acid with *p*-iodobenzoyl chloride, crystallises from hot water in plates and melts at 193°. The *nitrile* separates from alcohol in prismatic crystals and melts at 191—192°. The *ethyl* ester crystallises from alcohol in plates and melts at 128—129°. *Di*-p-*iodobenzoylaminoacetonitrile*,

$$(C_6H_4I\cdot CO)_2N\cdot CH_2\cdot CN,$$

obtained under certain conditions by the action of *p*-iodobenzoyl chloride on aminoacetonitrile sulphate in presence of sodium hydroxide, crystallises from alcohol in clusters of radiating prisms and melts at 215—216°.

p-*Iodobenzoylanilide*, $C_6H_4I\cdot CO\cdot NHPh$, melts at 210°. 3:5-*Dinitrobenzoylanilide*, $C_6H_3(NO_2)_2\cdot CO\cdot NHPh$, crystallises from alcohol in needles and melts at 234—235°. 3:5-*Dinitrobenzoyl*-p-*toluidide*, $C_6H_3(NO_2)_2\cdot CO\cdot NH\cdot C_6H_4Me$, does not melt below 280° and is practically insoluble in the usual solvents. 3:5-*Dinitrobenzoyl*-o-*toluidide* crystallises from alcohol and melts at 241—242°.

[With Walter C. Chalker.]—3:5-*Dinitrobenzoylmethylanilide*, $C_6H_3(NO_2)_2\cdot CO\cdot NPhMe$, separates from alcohol in prismatic crystals, and melts at 155—156°. 3:5-*Dinitrobenzoyldiphenylamide*,

$$C_6H_3(NO_2)_2\cdot CO\cdot NPh_2,$$

crystallises in prisms and melts at 180—181°. 3:5-*Dinitrobenzoyl*-α-*naphthylamide*, $C_6H_3(NO_2)_2\cdot CO\cdot NH\cdot C_{10}H_7$, melts at 268° and is insoluble in the ordinary solvents. E. G.

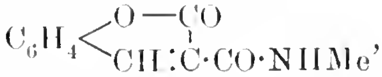
Decolorisation of a Faintly Alkaline Solution of Phenolphthalein by Alcohol.

Robert Cohn (*Zeit. angew. Chem.*, 1906, 19, 1389—1390).—The decolorisation produced by the addition of alcohol to a faintly alkaline solution of phenolphthalein is attributed to the diminution in the dissociation of the colouring matter. The fact that the colour is restored on warming and disappears again on cooling is explained by assuming that the dissociation varies directly with the temperature. The alcohol employed in these experiments was freshly distilled from alkali in order to ensure absence of acid, and it was demonstrated that the colour changes were not brought about by atmospheric carbon dioxide. P. H.

Preparation of the Amides of Coumarincarboxylic Acid.

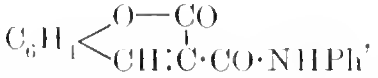
Emanuel Merck (D.R.-P. 172724).—Salicylaldehyde and malonamide were heated until the mixture became solid, when the product, after crystallisation from glacial acetic acid, separated in white, felted needles and melted at 268—269°. This substance, coumarincarboxyamide, is soluble in methyl and ethyl alcohols and ethyl acetate, but dissolves only sparingly in the other organic solvents.

Coumarincarboxymethylamide,



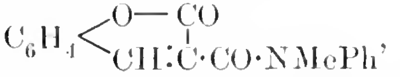
$C_6H_4<\begin{matrix}O—CO\\ CH:C\cdot CO\cdot NHMe\end{matrix}$, obtained from salicylaldehyde and *s*-malondimethylamide, crystallises from alcohol in long needles melting at 172—173°; it is soluble in chloroform, benzene, or toluene.

Coumarincarboxyanilide,



$C_6H_4<\begin{matrix}O—CO\\ CH:C\cdot CO\cdot NHPh\end{matrix}$, prepared by heating salicylaldehyde and malonanilide, forms long, yellow needles and melts at 250°; it dissolves readily in the acetone, ethyl acetate, glacial acetic acid, toluene, xylene, and the alcohols, and is only sparingly soluble in benzene, chloroform, light petroleum, or water.

Coumarincarboxymethylanilide,



$C_6H_4<\begin{matrix}O—CO\\ CH:C\cdot CO\cdot NMePh\end{matrix}$, crystallises from dilute alcohol in aggregates of white needles having a green reflex; it melts at 139—140°. G. T. M.

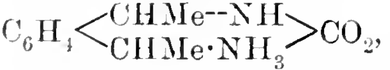
Decomposition of Ethyl Terephthalyldiacetoacetate and a Case of Stereoisomerism.

Ludwig Berend and Paul Herms (*J. pr. Chem.*, 1906, [ii], 74, 112—141).—*Ethyl terephthalyldiacetoacetate*, $C_6H_4(CO\cdot CHAc\cdot CO_2Et)_2$, prepared by gradually adding sodium ethoxide in absolute alcoholic solution and terephthalyl chloride in ethereal solution to ethyl acetoacetate, forms a white, fine crystalline powder, sinters at 90°, melts at 102·5°, is readily soluble in chloroform, acetone, benzene, ethyl acetate, or aqueous potassium hydroxide, and gives a red coloration with ferric chloride and a bluish-green precipitate with copper acetate. It is converted by the action of 10 per cent. alcoholic ammonia at 60° into acetamide and *ethyl terephthalyldiacetate*, $C_6H_4(CO{\cdot}CH_2{\cdot}CO_2Et)_2$, which crystallises from alcohol in large leaflets, melts at 70°, gives the characteristic colour reaction with ferric chloride, and, when heated with phenylhydrazine in glacial acetic acid solution on the water-bath, yields 3 : 3′-p-*phenylenedi*-1-*phenylpyrazolone*, $C_6H_4(C_3N_2H_2OPh)_2$; this melts at 284°, dissolves readily in hot aniline, nitrobenzene, or xylene, is soluble in aqueous sodium hydroxide, gives with copper salts a green, with uranium salts a brownish-red, or with cobalt salts a violet precipitate, and forms an *additive* compound with pyridine, which crystallises in large, white prisms and melts at 284—285°.

On prolonged boiling with water or very dilute sulphuric acid, ethyl terephthalyldiacetoacetate yields ethyl terephthalyldiacetate and benzoylacetylacetone; hydrolysis with 20 per cent. sulphuric acid leads to the formation of diacetylbenzene or, on prolonged boiling, of acetylbenzoic acid, whilst the products of the hydrolysis with 35 per cent. sulphuric acid are acetylbenzoic and terephthalic acids.

Terephthalyldiacetone, $C_6H_4(CO{\cdot}CH_2{\cdot}COMe)_2$, is formed synthetically by the action of ethyl terephthalate on acetone in presence of sodamide in absolute ethereal solution ; it crystallises in silvery leaflets, assumes a green lustre on repeated recrystallisation, and melts at 184°. It reacts with hydrazine hydrate in hot absolute alcoholic solution, forming p-*phenylenedi*-5-*methylpyrazole*,  $C_6H_4\left(C\begin{matrix}\diagup NH{\cdot}N \\ \diagdown CH{\cdot}CMe\end{matrix}\right)_2$, which crystallises from alcohol in stellate aggregates of needles, or from glacial acetic acid in leaflets, sinters at 327°, and melts and becomes brown at 332°.

Ethyl p-*acetylbenzoate*, $COMe{\cdot}C_6H_4{\cdot}CO_2Et$, prepared by the action of hydrogen chloride on the corresponding nitrile in absolute alcoholic solution, crystallises from water in white needles, melts at 57°, is sparingly soluble in boiling water, has an aromatic odour in aqueous solution, and is only slowly and incompletely volatile in a current of steam.

p-Diacetylbenzene is obtained in a 95 per cent. yield by boiling ethyl terephthalyldiacetate with 10 per cent. sulphuric acid ; the dioxime melts and decomposes at 240—245° (compare Ingle, Abstr., 1894, i, 589). p-*Phenylenedi-a-ethyldiamine* [p-*di-a-amino-diethylbenzene*] *hydrochloride*, $C_6H_4(CHMe{\cdot}NH_2,HCl)_2$, is prepared by reduction of the dioxime with sodium amalgam in acid solution and treatment of the base with hydrogen chloride in ethereal solution ; it does not melt or decompose in a capillary tube at 300°, but decomposes when heated on platinum, and is readily soluble in water or alcohol. The carbamate,  $C_6H_4{<}\begin{matrix}CHMe{-}NH \\ CHMe{\cdot}NH_3\end{matrix}{>}CO_2$, formed by passing carbon dioxide into the ethereal solution of the base, melts and decomposes at 85°, is soluble in water, and is decomposed by acids. i-p-Di-*a-aminodiethylbenzene*, $C_{10}H_{16}N_2$, is an oil which has a basic odour, distils without decomposition at about 140° under 12 mm. pressure, solidifies to transparent crystals when strongly cooled, and has $n_D = 1{\cdot}54126$ at 21·5°. The d-*tartrate*, formed by the action of *d*-tartaric acid on the carbamate, melts and decomposes at 186°, or, after repeated recrystallisations, at 193—194°; the base obtained from the first fraction has $[a]_D$ $-4°55{\cdot}8'$ at 22°, that from the last fraction $[a]_D - 5°2{\cdot}9'$ at 22°. The base obtained from the mother-liquors has $[a]_D + 18°8{\cdot}8'$ at 22°.

G. Y.

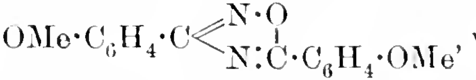
Action of Sodium Hypochlorite on Aldoximes. Giacomo Ponzio and G. Busti (*Atti R. Accad. Sci. Torino*, 1906, **41**, 862—868. Compare this vol., i, 482).—Further study of the action of sodium hypochlorite on the aldoximes shows that the latter, besides yielding peroxides of the form CHR:N·O·O·N:CHR, are partially converted into the corresponding azoximes,

$$\left.\begin{array}{l}CR{:}N\\ |\\ N{=}CR\end{array}\right\rangle O.$$

Thus, the interaction of sodium hypochlorite and benzaldoxime gives benzaldoxime peroxide and dibenzenylazoxime (compare Beckmann, Abstr., 1889, 980).

m-Nitrobenzaldoxime and sodium hypochloride yield: (1) di-*m*-nitrobenzenylazoxime, which melts at 169°; Stieglitz (Abstr., 1890, 254) gave the melting point as 168°, Krümmel (Abstr., 1895, i, 661) as 138°, Bamberger and Scheutz (Abstr., 1901, i, 548) as 147·5—149·5° and Franzen and Zimmermann (this vol., i, 388) as 184° (compare also Minunni and Ciusa, this vol., i, 187). (2) *m*-Nitrobenzaldoxime peroxide, melting at 131°; Minunni and Ciusa (*loc. cit.*) gave the melting point 105°, and Franzen and Zimmermann (*loc. cit.*) 124°.

Anisaldoxime and sodium hypochlorite yield: (1) *di*-p-*methoxybenzenylazoxime*,



$$OMe{\cdot}C_6H_4{\cdot}C\left\langle\begin{array}{l}N{\cdot}O\\ \quad\ \ |\\ N{:}C{\cdot}C_6H_4{\cdot}OMe\end{array}\right.$$

which crystallises from alcohol or acetic acid in flattened, shining, white needles melting at 175—176° and dissolves readily in chloroform and sparingly in ether. (2) Anisaldoxime peroxide (*p*-methoxybenzaldoxime peroxide), which melts at 126°; Franzen and Zimmermann (*loc. cit.*) gave the melting point 119·5°.

Furfuraldoxime peroxide, $O_2(N{:}CH{\cdot}C_4H_3O)_2$, prepared by the action of sodium hypochlorite or nitrous acid on furfuraldoxime, crystallises from chloroform in yellow plates which melt and decompose with a slight explosion at 130°.

T. H. P.

Piperonal and Hydrogen Chloride: a Two-component Three-phase System. Forris J. Moore (*J. Amer. Chem. Soc.*, 1906, **28**, 1188—1190).—When piperonal is treated with dry hydrogen chloride under a pressure of about one atmosphere, the gas is readily absorbed and a liquid additive *compound* is produced. On reducing the pressure, hydrogen chloride is rapidly evolved from the liquid and crystals of piperonal separate. A rough measurement has shown that the dissociation pressure is about 500 mm.

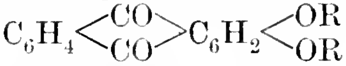
A description and diagram are given of an apparatus by means of which these changes can be demonstrated as a lecture experiment in illustration of the phase rule. E. G.

Relation between Colour and Constitution of Acids, Salts, and Esters.

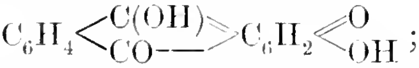
Arthur Hantzsch (*Ber.*, 1906, **39**, 3080—3102).—The term *chromo* is used in preference to *aci*. The prefix *mero* is applied to the names of faintly-coloured hydrogen compounds which consist of solid solutions of the coloured chromo-form in the colourless isomeride. A distinction is drawn between "farbig" and "gefärbt." The former is applied to substances with specific colour, whilst the latter denotes colourless compounds containing coloured impurities.

Constitutively unchangeable colourless acids produce not only colourless ions, but also colourless ethers, esters, and salts with colourless alkyl or acyl compounds and metals (the oxides of which are colourless) respectively. Constitutively unchangeable coloured acids produce coloured ions, ethers, esters, and salts.

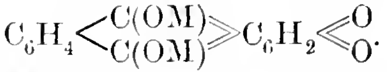
Substances with acidic character are arranged in four classes. (1) Hydrogen, alkyl, acyl, and metallic derivatives are colourless or equally coloured. Such acids are constitutively unchangeable. (2) The hydrogen and alkyl compounds are colourless, whilst the ions and salts exhibit colour. Such substances are pseudo-acids. (3) The hydrogen compound is *coloured*, the alkyl derivatives are colourless, and the ions and salts coloured. In these cases the alkyl compounds are derived from the pseudo-acid, the salts from the real acid, whilst the hydrogen derivative is a mero-compound. (4) This class is complicated and has not been examined thoroughly. Change of colour during salt formation is evidence of intramolecular change. Anthraquinone and its non-isomerisable derivatives, alizarin diacetate and dimethyl ether, are yellow, alizarin, which is capable of exhibiting tautomerism, is red, whilst the metallic derivatives are violet:



$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_2<\begin{matrix}OR\\OR\end{matrix}$;



$C_6H_4<\begin{matrix}C(OH)\\CO\text{——}\end{matrix}>C_6H_2<\begin{matrix}O\\OH\end{matrix}$;



$C_6H_4<\begin{matrix}C(OM)\\C(OM)\end{matrix}\geqslant C_6H_2\leqslant\begin{matrix}O\\O\end{matrix}$.

[With W. Prätorius and Edith Morgan.]—The alkyl and acyl derivatives of the hydroxybenzaldehydes are colourless. The presence of certain nuclear substituents, especially methoxyl or ethoxyl, may confer colour on the hydroxybenzaldehydes.

The salts and ions of *p*-hydroxybenzaldehyde and of its mono- and di-bromo-derivatives are colourless. The salts of the meta-isomeride are colourless when solid or in anhydrous solvents, but form yellow aqueous solutions. The *ammonium* salt, $CHO{\cdot}C_6H_4{\cdot}ONH_4$, is obtained from ammonia and the solid at the ordinary temperature, or in ethereal solution at $-40°$.

Salicylaldehyde yields the following colourless salts: the *acid potassium* salt, $CHO{\cdot}C_6H_4{\cdot}OK,C_7H_6O_2$, by the action of potassium ethoxide ($< \frac{1}{2}$ mol.) on an ethereal solution; the *acid sodium* salt,

$$CHO{\cdot}C_6H_4{\cdot}ONa,C_7H_6O_2,$$

in a similar manner with excess of sodium ethoxide. The *ammonium* salt, $CHO{\cdot}C_6H_4{\cdot}ONH_4$, obtained from ammonia and salicylaldehyde, dissolves in ether, toluene, or light petroleum, melts at 85°. In an atmosphere of ammonia or in alcoholic solution, it changes into hydrosalicylamide. It dissolves in liquid ammonia to an intensely yellow solution of the enolic form, $CH(ONH_4):C_6H_4:O$, but is recovered colourless after evaporation of the solvent.

Aqueous solutions of these colourless salts are intensely yellow, the colour deepening by warming. The acid sodium salt separates from water or dilute alcohol in yellow leaflets containing $\frac{1}{2}H_2O$.

The *potassium* salt, $O:C_6H_4:CH\cdot OK$, is precipitated from aqueous or alcoholic solution by potassium ethoxide (1 mol.). The *lead*, *mercury*, and *thallium* salts are coloured.

Mono- and di-bromosalicylaldehydes are colourless in non-dissociating solvents, and yellow in water or alcohol. The yellow *ammonium* salt, $O:C_6H_2Br_2:CH\cdot ONH_4$, obtained from ammonia and dibromosalicylaldehyde, solid or in indifferent solvents, can be crystallised from alcohol or ether; when heated it forms a brominated hydrosalicylamide. The *trimethylamine* and *α-piperidine* salts are yellow. Resorcinaldehyde and phloroglucinolaldehyde yield colourless alkali, and yellow lead, thallium, and mercury salts.

The yellow hydrosalicylamide (m. p. 160°) is a chromo compound, $N_2(:C_6H_4:CH\cdot OH)_3$. The colourless isomeride, $(OH\cdot C_6H_4\cdot CH:)_3N_2$, resulting from ammonia and the yellow form at −40°, has the same melting point.

[With M. B. BLACKLER.]—The influence of the nature and of the position of substituents on the colour of aromatic hydroxyketones is discussed.

Potassium p-*hydroxybenzophenone*, $C_{13}H_9O_2K$, prepared from potassium ethoxide and an ethereal solution of the ketone, contains 1 mol. C_2H_6O, which is lost over sulphuric acid. The salt is intensely yellow, as is also the *ammonium* salt.

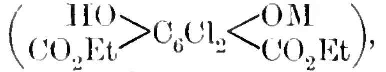
3-*Bromo*-4-*hydroxybenzophenone*, $C_{13}H_9O_2Br$, melts at 180—181°, forms colourless solutions in indifferent solvents, and yields a yellow *potassium* salt.

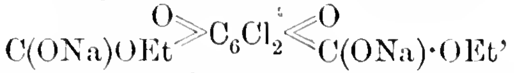
3:5-*Dibromo*-4-*hydroxybenzophenone*, $C_{13}H_8OBr_2$, melts at 151—152°, is colourless in all solvents, and forms colourless *potassium*, *barium*, *lead*, and *silver* salts.

2:4-Dihydroxyacetophenone forms colourless solutions in cold alkali hydroxides, which become yellow by warming. The solid *lead*, *silver*, and *mercuric* salts are colourless. 2:4-Dihydroxypropiophenone has been obtained in colourless crystals containing 1 mol., H_2O, and melting at 56°; the anhydrous substance melts at 97·5° and forms colourless salts.

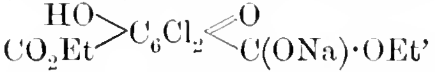
2-Hydroxy-5-methylbenzophenone is a merochromo-compound; the solution in light petroleum is colourless, but deposits yellow crystals. The acetyl and benzoyl derivatives, and the same compounds of all coloured aromatic hydroxyketones, are obtained colourless by treating the alkali salt suspended in ether or chloroform with the acid chloride.

2:5-Dimethoxybenzophenone has been obtained colourless. 2:1-Acetylnaphthol forms yellow solutions, except in light petroleum; the alkali and the barium salts are yellow, whilst the acetyl derivative which melts at 107·5°, and the benzoyl derivative, which melts at 131° (compare Ullmann, Abstr., 1897, i, 482), are colourless when prepared as described above. The corresponding ethyl ketone is obtained conveniently by treating a solution of zinc chloride in propionic acid with *α*-naphthol at 160—170°; its salts are yellow and the benzoyl derivative colourless. The brominated ketones form yellow needles and melt at 126—127° and at 98° respectively; their salts are yellow and the acetyl and benzoyl derivatives colourless.

The esters of the hydroxybenzoic acids and their derivatives do not form coloured salts. Selective absorption is first exhibited by the salts of acids containing two pairs of *o*-hydroxy and carbethoxy-groups. Ethyl dichloroquinoldicarboxylate forms colourless salts with tertiary amines  $\left(\begin{matrix}HO\\CO_2Et\end{matrix}\!>\!C_6Cl_2\!<\!\begin{matrix}OM\\CO_2Et\end{matrix}\right)$, *coloured* compounds with secondary amines, and the following coloured salts: *sodium* salt,



$$\begin{matrix}O\\C(ONa)OEt\end{matrix}\!>\!C_6Cl_2\!<\!\begin{matrix}O\\C(ONa)\cdot OEt\end{matrix},$$

obtained from an alcoholic solution of the ester and sodium ethoxide (2 mols.); similar *potassium* and *rubidium* salts; *acid sodium* salts,  $\begin{matrix}HO\\CO_2Et\end{matrix}\!>\!C_6Cl_2\!<\!\begin{matrix}O\\C(ONa)\cdot OEt\end{matrix}$, obtained in a similar manner with 1 mol. of sodium ethoxide; the yellow *ammonium* salt, $C_{12}H_{11}O_6Cl_2\cdot NH_4$, and the colourless salts with tertiary amines are obtained by the addition of ammonia or of the amine to an ethereal solution of the ester. The ester itself is colourless when solid or in cold alcoholic solution; when fused or in hot alcoholic solution, or in benzene or chloroform, it becomes greenish-yellow and is represented as a merochromo-compound. Similar colour relations are manifested by the salts of quinoldicarboxylic acid and its ethyl ester. C. S.

Methineammonium Dyes. III. Hans Rupe and O. Siebel (*Zeit. Farb. Ind.*, 1906, **5**, 301—304. Compare Abstr., 1904, i, 107; 1905, i, 83).—p-*Acetylaminobenzaldehyde*, $NHAc\cdot C_6H_4\cdot CHO$, prepared by warming *p*-aminobenzaldehyde with acetic anhydride, crystallises from toluene in yellow needles, melts at 141°, and condenses with acetone in presence of sodium hydroxide to form *acetyl*-p-*aminobenzylideneacetone*, $NHAc\cdot C_6H_4\cdot CH\colon CH\cdot COMe$; this crystallises from water in dull yellow needles, melts at 184°, and is hydrolysed by sulphuric acid in acetic acid solution, forming p-*aminobenzylideneacetone*, $NH_2\cdot C_6H_4\cdot CH\colon CH\cdot COMe$, which crystallises from 50 per cent. methyl alcohol in yellow leaflets and melts at 81°. The base is best prepared by condensing commercial aminobenzaldehyde dissolved in 50 per cent. acetic acid with acetone. On adding dilute hydrochloric acid gradually to a suspension of the base in water, a deep red solution is first produced, which becomes colourless on adding more acid; this behaviour characterises the methineammonium bases. The red solution has strong tinctorial properties. Coloured azo-compounds are formed on coupling diazotised *p*-aminobenzylideneacetone with hydroxy- and amino-naphthalene sulphonic acids. The *oxime*,

$$NH_2\cdot C_6H_4\cdot CH\colon CH\cdot CMe\colon N\cdot OH,$$

of the base, crystallises from alcohol and melts at 196°. The *benzoyl* derivative, $NHBz\cdot C_6H_4\cdot CH:CH\cdot COMe$, crystallises from alcohol in yellow needles and melts at 207°. The *thiocarbamide*,

$$CS(NH\cdot C_6H_4\cdot CH:CH\cdot COMe)_2,$$

is sparingly soluble in all solvents and melts at 162°. The *hydrazone*, $NH_2\cdot C_6H_4\cdot CH:CH\cdot CMe:N\cdot NH_2$, forms scaly leaflets and melts at 92°.

p-*Dimethylaminobenzylideneacetone*, $NMe_2\cdot C_6H_4\cdot CH:CH\cdot COMe$, prepared from dimethylaminobenzaldehyde and acetone at the ordinary temperature, crystallises from alcohol in feebly yellow leaflets and melts at 132°; the substance described under the same name by Sachs and Lewin (Abstr., 1903, i, 37) is probably a more complex condensation product. The *phenylhydrazone*, $NMe_2\cdot C_6H_4\cdot CH:CH\cdot CMe:N\cdot NHPh$, crystallises from alcohol and melts at 165°. The *oxime*,

$$NMe_2\cdot C_6H_4\cdot CH:CH\cdot CMe:N\cdot OH,$$

crystallises from alcohol in yellow leaflets and melts at 168°. p-*Dimethylamino*-p-*nitrodibenzylideneacetone*,

$$NMe_2\cdot C_6H_4\cdot CH:CH\cdot CO\cdot CH:CH\cdot C_6H_4\cdot NO_2,$$

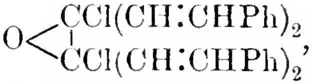
prepared by the condensation of dimethylaminobenzylideneacetone and *p*-nitrobenzaldehyde, crystallises from glacial acetic acid and melts at 215°; the *hydrochloride*, $C_{19}H_{18}O_3N_2,HCl$, is blue, and is decomposed by water. p-*Dimethylamino*-p-*aminodibenzylideneacetone*, obtained by the reduction of the nitro-compound, crystallises from alcohol in intensely red leaflets and melts at 228°. W. A. D.

Dibenzylideneacetone and Triphenylmethane. I. FRITZ STRAUS and O. ECKER (*Ber.*, 1906, 39, 2977—3006).—*Distyryldichloromethane*, $CCl_2(CH:CHPh)_2$, prepared by cautiously adding dry phosphorus pentachloride to a boiling solution of dibenzylideneacetone in benzene, forms clusters of silvery leaflets melting at 77°.

Distyryldichloromethane dichloride, $CHPhCl\cdot CHCl\cdot CCl_2\cdot CH:CHPh$, formed by adding a saturated chloroform solution of chlorine to the keto-chloride dissolved in the same solvent, crystallises from benzene and petroleum in radially-grouped needles melting at 133°. The corresponding *dibromide* crystallises in colourless prisms and melts and decomposes at 153°. Distyryldichloromethane when quite dry is not affected by hydrogen chloride, but when dissolved in cold concentrated sulphuric acid it gives a bluish-violet solution with reddish-violet fluorescence; the colour gradually changes to brownish-orange, especially on warming. Hydrogen chloride is evolved, and when the interaction is effected in carbon disulphide solution, the *sulphate*, $C_{17}H_{14}Cl\cdot SO_4H,H_2SO_4$, separates in violet crystals which are extremely sensitive to moisture. When treated with absolute ether, the violet crystals are decomposed, yielding dibenzylideneacetone and an oil containing chlorine. The keto-chloride readily dissolved in liquid sulphur dioxide, and the solution had an appreciable electrical conductivity, although not so great as that of triphenylchloromethane in the same solvent.

Distyryldichloromethane combines with metallic chlorides, the *stannichloride*, $C_{17}H_{14}Cl_2,SnCl_4$, forms violet leaflets with a bronzy lustre, the *mercurichloride* separates in violet-brown needles. Methyl alcohol attacks the keto-chloride, ultimately eliminating both chlorine atoms in the form of hydrogen chloride, and yielding a red, crystalline substance which could not be purified; glacial acetic acid also removes one chlorine atom, the product being probably the carbinol acetate, $C(CH{:}CHPh)_2Cl{\cdot}OAc$.

Two *distyrylchlorocarbinol anhydrides*,



$$O<\begin{matrix}CCl(CH{:}CHPh)_2\\ |\\ CCl(CH{:}CHPh)_2\end{matrix}$$

are produced on shaking an ethereal solution of distyryldichloromethane with water, the total yield being about 40—50 per cent. of the keto-chloride. The mixture, when crystallised from benzene and light petroleum, yields large, hard, transparent prisms decomposing violently at 147°, and slender, soft, light needles decomposing at 167—169°. The substances differ in their behaviour towards warm glacial acetic acid; the prismatic substance furnishes a solid product, $C_{35}H_{29}OCl$, melting at 159—161°, whilst the acicular compound yields an oil.

Di-p-chlorobenzylideneacetone, $CO(CH{:}CH{\cdot}C_6H_4Cl)_2$, prepared by condensing *p*-chlorobenzaldehyde and acetone in dilute alcoholic solution in the presence of sodium hydroxide, crystallises in well-defined yellow leaflets and melts at 193°.

Di-p-chlorostyryldichloromethane, $CCl_2(CH{:}CH{\cdot}C_6H_4Cl)_2$, obtained from the preceding compound by the action of phosphorus pentachloride in benzene solution, crystallises from ether in radial aggregates of thick, colourless prisms melting at 102—103°.

The *dibromide*, $C_6H_4Cl{\cdot}CHBr{\cdot}CHBr{\cdot}CCl_2{\cdot}CH{:}CH{\cdot}C_6H_4Cl$, was obtained by treating the keto-chloride with bromine; it crystallises from benzene and petroleum in aggregates of colourless needles melting at 124—125°.

The *stannichloride*, $C_{17}H_{12}Cl_4,SnCl_4$, separates in fine, crystalline aggregates having a metallic lustre.

The *methyl ether* of *di-p-chlorostyrylchlorocarbinol*,

$$OMe{\cdot}CCl(CH{:}CH{\cdot}C_6H_4Cl)_2,$$

formed by adding a benzene solution of the keto-chloride to a methyl alcohol solution of sodium methoxide, separates from methyl alcohol in aggregates of white needles melting at 95—96·5°. It was not found possible to replace the second chlorine atom by methoxyl, neither could this halogen be removed by reducing agents.

Di-p-iodobenzylideneacetone, $CO(CH{:}CH{\cdot}C_6H_4I)_2$, was prepared by condensing *p*-iodobenzaldehyde and acetone in the presence of alkalis; when crystallised from pyridine, it separated in yellow leaflets melting at 254—255°. This ketone is sparingly soluble in the ordinary organic media.

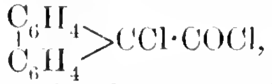
Di-p-iodostyryldichloromethane, $CCl_2(CH{:}CH{\cdot}C_6H_4I)_2$, crystallises from petroleum in white, crystalline masses or from benzene in white needles melting at 146—147°.

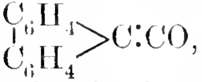
Dianisylideneacetone and phosphorus pentachloride in benzene solution furnish the *compound* $CCl_2(CH{:}CH{\cdot}C_6H_4{\cdot}OMe)_2,PCl_5,C_6H_6$, which separates in green leaflets. When the benzene solution of phosphorus pentachloride and dianisylideneacetone is heated for half an hour, the liquid no longer deposits the green compound on cooling; but on evaporation a grey, crystalline mass is obtained which, after purification, crystallises from carbon disulphide in colourless prisms melting and decomposing at 106—107°. This *compound* is probably

$$OMe\cdot C_6H_4\cdot CHCl\cdot CHCl\cdot CCl_2\cdot CH{:}CH\cdot C_6H_4\cdot OMe.$$

Benzophenone dichloride, when treated with methyl alcohol, furnishes dimethoxydiphenylmethane.

The characteristic behaviour of many of these chloro-derivatives with sulphuric acid is described in detail. G. T. M.

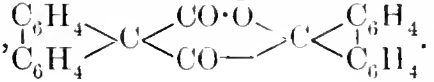
Ketenes. III. Diphenyleneketene. HERMANN STAUDINGER (*Ber.*, 1906, **39**, 3062—3067. Compare Abstr., 1905, i, 444; this vol., i, 234).—*Chlorodiphenyleneacetyl chloride*,  $\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!>\!CCl\cdot COCl$, is formed in 50 per cent. yield when phosphorus pentachloride reacts with diphenyleneglycollic acid in cold chloroform; it melts at 111·5—112·5°, and reacts with water to regenerate the acid, with alcohol to form ethyl chlorodiphenyleneacetate, which melts at 46—47°, and with aniline to form the *anilide*, $C_{20}H_{14}ONCl$, which melts at 177°.

Diphenyleneketene,  $\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!>\!C{:}CO$, obtained by the action of zinc on the preceding chloride in ether in the absence of air and moisture, melts at 90—90·5° to a red liquid, decomposes at 150°, and gives an indigo blue coloration with concentrated sulphuric acid. With excess of water it yields diphenyleneacetic acid, whilst the addition of the requisite amount of water to the ketene dissolved in benzene or light petroleum precipitates the *anhydride*, $C_{28}H_{18}O_3$, which melts at 164—165°.

Ethyl diphenyleneacetate, prepared from the ketene and ethyl alcohol, or by esterifying the acid, melts at 43—45° and boils at 209—210° under 17 mm. pressure. The *anilide*, $C_{20}H_{15}ON$, separates from xylene in slender needles and melts at 255°; the *phenylhydrazide* melts at 234—235°.

From solutions of the ketene in light petroleum, tertiary bases such as quinoline, quinaldine, pyridine, or triethylamine precipitate additive compounds which are decomposed by water; the quinoline *compound*, $2C_{14}H_8O,C_9NH_7$, is a white, crystalline powder which darkens at 140° and melts and decomposes at 154—155°. These additive compounds are stable to oxygen, but behave like the ketenes to water, alcohol, aniline, phenylhydrazine, and the Schiff bases. The quinoline compound reacts with water to form a mixture of diphenyleneacetic acid and *quinoline diphenyleneacetate*, $C_{14}H_{10}O_2,C_9NH_7$; the latter melts at 109—110°.

Bisdiphenyleneallene,  $\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!>\!C{:}C{:}C\!<\!\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}$, forms orange-yellow needles and is obtained by heating the quinoline additive compound with quinoline diphenyleneacetate.

The zinc chloride precipitated in the preparation of diphenyleneketene contains a considerable quantity of the ketene. When the precipitate is oxidised by atmospheric oxygen, fluorenone and a *substance*, $C_{28}H_{16}O_3$, which melts at 269—270° are obtained; the latter is regarded as a tetra-substituted derivative of tetronic acid,  $\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!>\!C\!<\!\begin{matrix}CO\cdot O\\ CO—\end{matrix}\!>\!C\!<\!\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}$.

C. S.

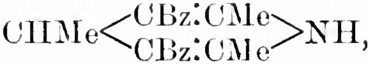
Derivatives of Benzoylacetone. GIOVANNI ISSOGLIO (*Atti R. Accad. Torino*, 1906, 41, 946—960).—When benzoylacetone is treated with acetaldehyde in presence of concentrated ammonia solution, it reacts as if it possessed the enolic structure of β-hydroxy-α-benzoylpropylene, $OH\cdot CMe\colon CHBz$, the following products being obtained.

(1) *Dibenzoyldiisopropylamine*, $NH(CHMe\cdot CH_2Bz)_2$, crystallises from benzene in shining, rhombic plates melting at 127°, dissolves in alcohol or chloroform, and to a slight extent in ether, and has the normal molecular weight in freezing benzene. The *platinichloride*,

$$(C_{20}H_{23}O_2N)_2,H_2PtCl_6,$$

forms an amorphous precipitate melting at 198°, and the *picrate*, $C_{20}H_{23}O_2N,C_6H_2(NO_2)_3\cdot OH$, crystallises in microscopic, fern-like aggregates of yellow needles melting and decomposing at 192°.

(2) *β-Ethylidenedibenzoylacetone*, $CHAcBz\cdot CHMe\cdot CBz\colon CMe\cdot OH$, crystallises from 60 per cent. alcohol in white needles with a silvery lustre, melts at 134°, and dissolves readily in alcohol, acetone, or chloroform, and less so in benzene.

(3) 3 : 5-*Dibenzoyl*-2 : 4 : 6-*trimethyl*-1 : 4-*dihydropyridine* (3 : 5-*dibenzoyl*-1 : 4-*dihydrocollidine*),  $CHMe<\begin{matrix}CBz\colon CMe\\CBz\colon CMe\end{matrix}>NH$, crystallises from alcohol in slender, straw-yellow needles, begins to turn brown at 200°, and melts at 238—239°, and is slightly soluble in acetone, chloroform, or benzene. T. H. P.

The Employment of Vanadium Salts in the Electrolytic Oxidation or Reduction of Organic Compounds. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 172654).—Vanadium salts are very suitable depolarisers either at the anode or cathode, and the attack of the oxygen or hydrogen on the organic substance is greatly accelerated.

Finely-pulverised anthracene (4 kilograms) is introduced into a leaden anode cell containing 100 litres of 20 per cent. sulphuric acid with 3 per cent. of vanadic acid. The current density is 300 amperes per square metre with 1·8 volts. After filtering off the anthraquinone, which is rapidly produced in good yield, the electrolytic solution is ready for a further quantity of anthracene.

By the aid of vanadium salts, aniline may be oxidised to benzoquinone, and the latter then reduced to quinol. Azobenzene and azoxybenzene suspended in 20 per cent. sulphuric acid containing two parts of vanadium trioxide are reduced to benzidine in the cathode cell. G. T. M.

Preparation of Derivatives of the Reduction Products of Anthraquinone. BADISCHE ANILIN- UND SODA-FABRIK (D.R.-P. 172930).—The reduction products of anthraquinone, anthranol, hydroxyanthranol and their homologues and sulphonic acids condense with aldehydes to yield substances which are insoluble in alkalis.

Anthranol, when condensed with benzaldehyde in concentrated sulphuric acid at 30—35°, yields a substance which, when crystallised from alcohol, separates in needles melting at 112—114°; this compound is indifferent towards dilute acids or alkalis, but develops a magenta coloration with concentrated sulphuric acid. A similar substance can be obtained with hydroxyanthranol.

Anthranol also condenses with para-acetaldehyde: the product is an olive-yellow powder, insoluble in dilute acids or alkalis, but dissolving in concentrated sulphuric acid to a reddish-brown, fluorescent solution.

G. T. M.

Preparation of the Urethanes of Polynitroaminoanthraquinones. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 171588).—It is not possible to introduce into the aminoanthraquinones and their acetyl derivatives more than one nitro-group, and only two of these groups can be introduced into the diaminoanthraquinones and their diacetyl compounds. The urethanes of these amino- and diamino-anthraquinones, on the other hand, can be nitrated readily to furnish polynitro-derivatives which on hydrolysis yield polynitroaminoanthraquinones of great technical importance. The hydrolysis is carried out by heating the nitrated urethane in concentrated sulphuric acid at 80° until the evolution of carbon dioxide ceases. In this way, the following compounds were prepared: 2 : 4-*dinitro*-1-*aminoanthraquinone*, 1 : 3-*dinitro*-2-*aminoanthraquinone*, 2 : 4 : 6 : 8-*tetranitro*-1 : 5-*diaminoanthraquinone*, and 2 : 4 : 5 : 7-*tetranitro*-1 : 8-*diaminoanthraquinone*.

These compounds develop characteristic colorations when dissolved in pyridine, concentrated and fuming sulphuric acid, or in a mixture of sulphuric and boric acids.

G. T. M.

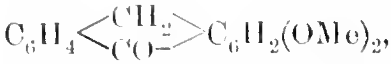
Methylation of Hydroxyanthraquinones. CARL GRAEBE (*Annalen*, 1906, **349**, 201—207. Compare Abstr., 1905, i, 219).—An introduction to the two papers following.

A hydroxy-group in position 1 in anthraquinone is either not methylated or is only very slightly methylated by methyl iodide. A more complete methylation is accomplished by acting on the deoxy-compound, which is afterwards readily oxidised to the anthraquinone ether.

The action of fuming sulphuric acid on alizarin, followed by heating the product with concentrated sulphuric acid, leads to the formation of quinalizarin, hydroxyanthrarufin (which is isolated from the residue by means of boiling toluene, crystallises in red needles, melts at 270—273°, and gives a violet coloration with sodium hydroxide or concentrated sulphuric acid) and 1 : 2 : 5-*trihydroxyanthraquinone-sulphonic acid*, $C_{14}H_8O_8S$, which is obtained also on prolonged heating of quinalizarin with sulphuric acid; it is obtained as a reddish-yellow precipitate, gives with alkali hydroxides a violet, with acetates a yellowish-red coloration, and yields hydroxyanthrarufin when heated alone or with hydrochloric acid at 180—200°.

G. Y.

Ethers of Alizarin, Flavopurpurin, Hydroxyanthrarufin, and Hydroxychrysazin. CARL GRAEBE and CARLOS THODE (*Annalen*, 1906, **349**, 207—222. Compare preceding abstract, Abstr., 1905, i, 219; Farbenfabriken vorm. Fr. Bayer & Co., Abstr., 1905, i, 362, 532).—*Deoxyalizarin dimethyl ether* (1 : 2-*dimethoxyanthrone*),



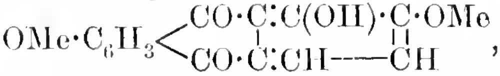
$C_6H_4<\begin{matrix}CH_2\\CO\end{matrix}>C_6H_2(OMe)_2$, prepared by the action of methyl sulphate on deoxyalizarin in 10 per cent. aqueous sodium hydroxide, crystallises in yellow needles, melts at 150°, forms a yellow solution in alcohol or benzene, showing a blue fluorescence when very dilute, and gives a yellow to yellowish-brown coloration with concentrated sulphuric acid. It is insoluble in aqueous sodium hydroxide, is only slowly attacked by boiling alkali hydroxides, remains unchanged when heated with 78 per cent. sulphuric acid at 100°, and does not form an acetyl derivative or an oxime. The *diethyl ether*, $C_{18}H_{18}O_3$, crystallises in yellow needles, melts at 128°, gives a yellow to yellowish-brown coloration with concentrated sulphuric acid, and on oxidation yields alizarin diethyl ether.

Alizarin 2-monomethyl ether is formed in small quantity, together with the dimethyl ether, by the action of methyl sulphate on alizarin; it is separated from the dimethyl ether by shaking the benzene solution with aqueous sodium hydroxide. It is obtained also by hydrolysis of the dimethyl ether with sulphuric acid on the water-bath.

Reduction of alizarin dimethyl ether by means of zinc dust and ammonia leads to the formation of deoxyalizarin dimethyl ether, together with an impure *ether*, which is formed also by reduction of deoxyalizarin dimethyl ether, melts at a lower temperature, and on oxidation with chromic acid and glacial acetic acid yields alizarin dimethyl ether.

Alizarin diethyl ether, $C_{18}H_{16}O_4$, prepared in a 2 per cent. yield, together with a 5 per cent. yield of the 2-monoethyl ether, by the action of ethyl sulphate on alizarin in aqueous sodium hydroxide solution on the water-bath, crystallises in yellow needles, melts at 162°, and yields the 2-monoethyl ether when heated with 78—80 per cent. sulphuric acid on the water-bath. The descriptions of the diethyl ether given by previous authors are erroneous.

Flavopurpurin-2 : 6-dimethyl ether,

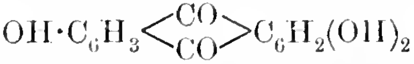


$$OMe\cdot C_6H_3<\begin{matrix}CO\cdot C\colon C(OH)\cdot C\cdot OMe\\ \quad\ \ |\qquad\qquad\quad \|\\ CO\cdot C\colon CH\text{———}CH\end{matrix},$$

prepared by heating the sodium derivative of flavopurpurin with methyl sulphate at 160°, or by heating the trimethyl ether with sulphuric acid at 100°, crystallises from a mixture of chloroform and carbon disulphide in yellow needles, melts at 239°, forms yellow solutions, is extracted from its solution in benzene or chloroform when shaken with aqueous sodium hydroxide, and forms a red *sodium* derivative and an *acetyl* derivative, $C_{18}H_{14}O_6$, which crystallises from glacial acetic acid and melts at 210°.

Deoxyflavopurpurin forms a yellow, crystalline precipitate and melts at 258°; when heated with methyl sulphate and 10 per cent. sodium hydroxide in an atmosphere of coal gas and oxidised with sodium dichromate and glacial acetic acid, it forms flavopurpurin trimethyl ether, melting at 225—226°, in a 30 per cent. yield.

Hydroxyanthrarufin (1 : 2 : 5-trihydroxyanthraquinone),



$$OH\cdot C_6H_3<\begin{matrix}CO\\CO\end{matrix}>C_6H_2(OH)_2$$

(compare Graebe. Abstr., 1891, 463), prepared by heating anthrarufin with sodium nitrate and aqueous sodium hydroxide under pressure at 180—185°, crystallises from glacial acetic acid in yellow or brownish-red needles, melts at 273—274°, forms a violet solution in aqueous alkali hydroxides, gives with concentrated sulphuric acid a violet coloration becoming blue on addition of boric acid, and shows a spectrum with three dark bands of 645—625, 590—570, and 545—530λ respectively; it dyes mordanted cotton, colours resembling those obtained with alizarin, but more bluish-red when the mordant is alumina. The *triacetate*, $C_{20}H_{11}O_8$, crystallises from alcohol in yellow needles and melts at 229°. The 2-*methyl ether* of hydroxyanthrarufin, $C_{15}H_{10}O_5$, formed by the action of methyl sulphate and sodium hydroxide on hydroxyanthrarufin, is obtained as a yellow precipitate, melts after recrystallisation from alcohol at 202°, and is not a dye. 1 : 2 : 5-*Trihydroxyanthrone* (*deoxyhydroxyanthrarufin*), $C_{14}H_{10}O_4$, prepared by reduction of hydroxyanthrarufin with zinc dust in dilute ammoniacal solution, melts at 258°; when treated with methyl sulphate and 4½ mols. of sodium hydroxide, it yields a *monoethyl ether*, $C_{15}H_{12}O_4$, which crystallises from alcohol and melts at 140°.

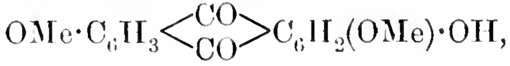
Hydroxychrysazin (1 : 2 : 8-trihydroxyanthraquinone) crystallises in orange needles, melt at 230° (corr.), forms solutions similar to those of anthrapurpurin, dyes cotton-wool mordanted with alumina brownish-red, or with iron a violet-grey, and gives with sulphuric acid a red coloration becoming violet on addition of boric acid. The triacetate melts at 218—219° (compare Liebermann and Giesel, this Journal, 1876, i, 711). On reduction with zinc dust and ammonia on the water-bath, treatment with methyl sulphate and sodium hydroxide, and oxidation with sodium dichromate in boiling glacial acetic acid solution, hydroxychrysazin forms the *trimethyl ether*, $C_{17}H_{14}O_5$, which crystallises from methyl alcohol, melts at 157°, and is soluble in benzene or chloroform, but is insoluble in aqueous sodium hydroxide. When heated with sulphuric acid on the water-bath, it is hydrolysed principally to the *dimethyl ether*, $C_{16}H_{12}O_5$, forming yellow crystals and melting at 193°, together with small quantities of the 2-*monomethyl ether*, $C_{15}H_{10}O_5$; this is prepared by the action of methyl sulphate on hydroxychrysazin in alkaline solution, crystallises in orange-yellow needles, melts at 220°, and is soluble in aqueous sodium hydroxide, but not in the carbonate.

G. Y.

Methyl Ethers of 2- and 1-Hydroxyanthraquinones, Anthrapurpurin, Purpurin, and Purpuroxanthin. CARL GRAEBE and HEINRICH BERNHARD (*Annalen*, 1906, **349**, 222—231. Compare preceding abstracts).—2-Methoxyanthraquinone, formed by the action of methyl sulphate on 2-hydroxyanthraquinone in alkaline solution, is identical with Kaufler's product from 2-nitroanthraquinone (Abstr., 1904, i, 256).

1-Methoxyanthraquinone is formed only in small quantities by the action of methyl sulphate on erythroxyanthraquinone, but in better yields by the action of methyl sulphate at 100°, or of potassium methyl sulphate at 200°, on the sodium derivative of erythroxyanthraquinone, or by successive reduction of the anthraquinone with zinc dust and glacial acetic acid, methylation, and oxidation; it crystallises from alcohol, melts at 169·5°, and is more stable than alizarin dimethyl ether towards sulphuric acid, being hydrolysed to 1-hydroxyanthraquinone only very slowly. 1-*Methoxyanthrone*, $C_{15}H_{10}O_2$, melts at 105°.

Anthrapurpurin melts at 369°, the *triacetate*, $C_{20}H_{14}O_8$, melts at 223—224°. The 2 : 7-*dimethyl ether*,



$$OMe\cdot C_6H_3{<}{}^{CO}_{CO}{>}C_6H_2(OMe)\cdot OH,$$

prepared by the action of an excess of methyl sulphate and sodium hydroxide on anthrapurpurin, or by the action of 78 per cent. sulphuric acid on anthrapurpurin trimethyl ether on the water-bath, crystallises from benzene, melts at 241°, and forms a red *sodium* derivative.

The *trimethyl ether* of anthrapurpurin, $C_{17}H_{14}O_5$, prepared by methylation and oxidation of deoxyanthrapurpurin, crystallises from alcohol in yellow needles, melts at 201°, and is readily soluble in benzene, chloroform, or hot alcohol.

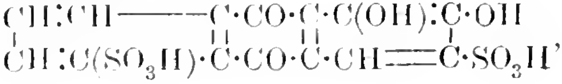
The action of an excess of sodium hydroxide and methyl sulphate on purpurin leads to the formation of the 2-monomethyl ether. The 3-methyl ether of purpuroxanthin, $C_{15}H_{10}O_4$, formed by the action of methyl sulphate and sodium hydroxide on purpuroxanthin, crystallises from benzene and melts at 193°; the benzene mother liquors contain a dimethyl ether crystallising in yellow needles and melting at 150—153° (compare Boeck, Abstr., 1905, i, 531). G. Y.

Conversion of Aromatic Ketones into the Corresponding Imides. Maurice Prud'homme (*Bull. Soc. chim.*, 1906, [iii], **35**, 666—668. Compare this vol., i, 193).—Hydroxyanthraquinones may be readily converted into the corresponding imides by heating them in glycerol with a normal ammonium salt of an organic acid or with ammonium carbonate. Under similar conditions, tetramethyldiaminobenzophenone furnishes auramine. "Alizarin yellows A and C," when treated in this way, yield products giving yellow and olive tints with the usual mordants, which are different from those given by the original dyes.

When alizarin is fused with ammonium thiocyanate in place of ammonium carbonate, or sulphur is added to a mixture of alizarin, glycerol, and the organic ammonium salt used to produce alizarinimide in the above reaction, the sulphur appears to enter into combination and to modify the tinctorial properties of the alizarinimide formed. T. A. H.

Preparation of Hydroxyanthraquinonesulphonic Acids. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 172688. Compare Abstr., 1905, i, 146).—The treatment of anthraquinone-*a*-sulphonic acid with fuming sulphuric acid containing a high percentage of sulphur trioxide leads to the introduction of hydroxyl groups into the anthracene nucleus. It is now found that the same result is obtained when acid containing less than 45 per cent. of sulphur trioxide is employed either with or without boric acid. Small quantities of mercury salts are found in many cases to accelerate the oxidation.

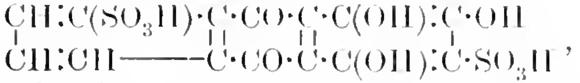
Alizarin-3 : 5-disulphonic acid,



$$\begin{array}{l} CH{:}CH\text{———}C\cdot CO\cdot C\cdot C(OH){:}C\cdot OH \\ CH{:}C(SO_3H)\cdot C\cdot CO\cdot C\cdot CH{=\!=}C\cdot SO_3H \end{array}$$

is produced by heating at 130—135° a mixture of potassium anthraquinone-*a*-sulphonate, boric acid, and fuming sulphuric acid containing 40 per cent. of sulphur trioxide. The *acid potassium* salt of alizarin-3 : 5-disulphonic acid crystallises on pouring the acid fusion into ice-cold water, whilst the quinizarin-*a*-sulphonic acid also produced in this reaction remains in solution and is precipitated with sodium chloride. Alizarin-3 : 5-disulphonic acid, when heated at 180° with 70 per cent. sulphuric acid, yields alizarin-5-sulphonic acid.

Purpurin-3 : 8-disulphonic acid,



$$\begin{array}{l} CH{:}C(SO_3H){\cdot}C{\cdot}CO{\cdot}C{\cdot}C(OH){:}C{\cdot}OH \\ CH{:}CH\text{——}C{\cdot}CO{\cdot}C{\cdot}C(OH){:}C{\cdot}SO_3H \end{array},$$

is produced by heating potassium anthraquinone-1 : 5-disulphonate with boric acid and fuming sulphuric acid (40 per cent. SO_3), under 6 to 7 atmospheres pressure. When poured into water, the fusion yields the *acid potassium* salt of this acid, which, when crystallised from dilute hydrochloric acid, separates in yellowish-red leaflets or prisms having a bronzy lustre. When heated at 180° with 70 per cent. sulphuric acid, the foregoing disulphonic acid furnishes purpurin-*a*-sulphonic acid; if a mercury salt is added, purpurin itself is formed.

Other di- and tri-hydroxyanthraquinonesulphonic acids can be prepared similarly by the foregoing process, and the properties of some of these products are tabulated in the patent. G. T. M.

Preparation of Chlorinated Quinazarins. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 172105).—Chlorinated quinazarins may be prepared by condensing quinol with those chlorophthalic acids which contain not more than one halogen atom in an ortho-position with respect to the carboxyl groups.

Quinol and 4 : 5-dichlorophthalic anhydride are heated at 155—160° for four hours in concentrated sulphuric acid, either alone or with the addition of boric acid; the product is poured into water, dissolved in an aqueous alkali hydroxide and reprecipitated by dilute acid. When crystallised from glacial acetic acid, it separates in brownish-red leaflets melting at 255°. Its solutions are bluer than those of quinazarin itself; that in concentrated sulphuric acid assumes a yellow fluorescence on the addition of boric acid.

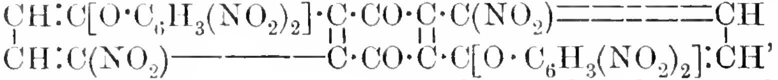
5-*Chloroquinazarin*, obtained from quinol and 3-chlorophthalic acid, crystallises from glacial acetic acid in brownish-red needles melting at 240°. G. T. M.

Bluish-green Colouring Matters of the Anthracene Series. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 172575).—When dinitroanthrarufindisulphonic acid is reduced with alkali sulphides in alkaline solutions, the reaction leads readily to the formation of diaminoanthrarufindisulphonic acid. If, however, the nitrosulphonic acid is reduced with sulphide in neutral solution, then beside the diamino-derivative a new product is formed, and this is obtained exclusively when alkali hydrosulphide is used instead of a sulphide. Although the exact nature of this new substance has not yet been ascertained, it is probably a partial reduction product such as a hydroxylamino- or a nitroamino-derivative, but it has not yet been

found possible to complete its reduction to diaminoanthrarufindisulphonic acid (Alizarinsaphirol *β*). The new product differs from the diamino-derivative in several of its colour reactions and also in tinctorial properties. These characteristic differences are arranged in the patent in tabular form.
G. T. M.

Preparation of *p*-Nitro-derivatives of the *α*-Hydroxyanthraquinones. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 170728).—The nitration of the *α*-hydroxyanthraquinones themselves leads to the production of a complex mixture of isomerides of which only the *p*-nitro-derivatives are of technical importance. It is therefore preferable to nitrate the aryl ethers of the *α*-hydroxyanthraquinones, as on hydrolysis the nitro-compounds thus obtained yield exclusively the required *p*-nitro-derivatives.

The diphenyl ether of anthrarufin on nitration yields the hexanitro-compound,



$$\begin{array}{l} \mathrm{CH{:}C[O{\cdot}C_6H_3(NO_2)_2]{\cdot}C{\cdot}CO{\cdot}C{\cdot}C(NO_2)}=\!=\!=\!=\!=\!=\mathrm{CH} \\ \mathrm{CH{:}C(NO_2)}-\!-\!-\!-\!-\!-\mathrm{C{\cdot}CO{\cdot}C{\cdot}C[O{\cdot}C_6H_3(NO_2)_2]{:}CH} \end{array}$$

, which on alkaline hydrolysis gives rise to 2 : 4-dinitrophenol and *p*-dinitroanthrarufin.

The diphenyl ester of chrysazin gives a similar hexanitro-compound which on hydrolysis furnishes 2 : 4-dinitrophenol and *p*-dinitrochrysazin.
G. T. M.

Preparation of Dichlorochrysazin. R. WEDEKIND & CO. (D.R.-P. 172300).—Chrysazin is not affected by chlorinating agents at 100°, but when 10 parts of this substance are suspended in 1000 parts of concentrated sulphuric acid diluted with their own weight of water and heated at 125°, while a solution of 20 parts of potassium chlorate and 80 parts of sodium chloride also dissolved in the same quantity of water is slowly added, chlorination takes place readily, and *pp*-dichlorochrysazin separates in well-defined orange-coloured crystals.
G. T. M.

Preparation of 1 : 2 : 2′ : 1′-Anthrazine. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 172684).—1 : 2 : 2′ : 1-Anthrazine, which was formerly obtained with great difficulty by the reduction of indanthrene, a substance formed by fusing *β*-aminoanthraquinone with alkali hydroxides, is now prepared by heating *β*-anthramine with a mixture of sodium and potassium hydroxides at 220—230° in the absence of air. The anthrazine, which forms a dark layer on the alkali, is easily separated and obtained pure by recrystallisation from nitrobenzene.
G. T. M.

Thioborneol. WALTHER BORSCHE and W. LANGE (*Ber.*, 1906, **39**, 3268).—Thioborneol, described recently by the authors (this vol., i, 679), had been obtained previously by Wuyts (Abstr., 1903, i, 428).
C. S.

Artificial Production of Camphor from Turpentine Oil. OTTO SCHMIDT (*Chem. Centr.*, 1906, ii, 722; from *Chem. Ind.*, **29**, 241—244).—The yield of camphor obtained by initially treating the crude oil with hydrochloric acid is very nearly the same (25 per cent.) as that obtained by the use of oxalic or salicylic acid. The conversion of pinene into bornyl and *iso*bornyl esters is readily effected by means of *o*-chlorobenzoic acid, which is more stable than salicylic acid and, therefore, to be preferred to the latter. H. M. D.

The Isolation of ψ-Ionone Hydrate and an Isomeride. P. Coulin (D.R.-P. 172653).—When moderately concentrated acids act on ψ-ionone even at the ordinary temperature, there is produced, together with ionone, hydrocarbons and tarry matters, a certain amount of substances, the boiling points of which are higher than those of ionone, ψ-ionone, or the hydrocarbons. It is now shown that this mixture contains ψ-ionone hydrate and an isomeride, $C_{13}H_{22}O_2$, and that these two compounds can be separated by means of alkali sulphites, in solutions of which the ψ-ionone hydrate readily dissolves, whilst its isomeride is insoluble. This isomeric substance is a viscid oil boiling at 166·8° to 169·8° under 10·5 mm. pressure and having a refractive index 1·50647 at 21°; it slowly solidifies to a crystalline mass melting at 80°; its *semicarbazone*, which is formed quantitatively, crystallises readily and melts and decomposes at 228°.

The ψ-ionone hydrate is isolated from the sodium sulphite solution by making this strongly alkaline and extracting with ether or benzene; it boils at 180—182° under 12 mm. pressure, and has a sp. gr. 0·954 at 15° and n_D 1·53322 at 20°. G. T. M.

Oils from Conifers. R. E. Hanson and E. N. Babcock (*J. Amer. Chem. Soc.*, 1906, **28**, 1198—1201).—The following volatile oils, with the exception of the first two and the last, are now described for the first time.

The leaves of the black spruce (*Picea Mariana*) yield 0·57 per cent. of an oil which has a sp. gr. 0·9274 at 19°.

Samples of oil distilled from the leaves and twigs of the hemlock (*Tsuga canadensis*) were obtained in yields of 0·4 and 0·46 per cent., and had a sp. gr. 0·9238 and 0·9273 respectively at 15°.

The leaves of the cat spruce (*Picea canadensis*) yield 0·103 per cent. of an oil which has a sp. gr. 0·9216 at 15°, and contains 25·7 per cent. of esters (calculated as bornyl acetate).

The leaves of the red spruce (*Picea rubens*) furnish 0·204 per cent. of an oil which has an agreeable odour and a sp. gr. 0·9539 at 16°, and contains 7·76 per cent. of borneol and 66·2 per cent. of bornyl acetate.

The leaves and twigs of the American larch (*Larix americana*) yield 0·149 per cent. of an oil which has a sp. gr. 0·8816 at 15° and consists chiefly of pinene together with 15·1 per cent. of esters (calculated as bornyl acetate).

The cones of *Picea rubens* yield 0·38 per cent. of a golden-yellow oil which has a sp. gr. 0·8600 at 15°.

The cones of *Picea canadensis* yield 0·25 per cent. of a yellow oil which has a limonene-like odour and a sp. gr. 0·899 at 15°.

The leaves and twigs of the pitch pine (*Pinus rigida*) furnish a very small quantity (0·2 c.c. from 12 kilograms) of a yellow oil which has an extremely pungent odour.

The red pine (*Pinus resinosa*) yields about 0·001 per cent. of a pungent, brown oil.

The leaves and twigs of *Juniperus communis* furnish 0·15—0·18 per cent. of a light yellow oil which has a sp. gr. 0·8531 at 20°.

The oil distilled from the leaves of *Juniperus virginiana* has a sp. gr. 0·900 at 16°. E. G.

Action of Phenols and Naphthalene on Copals. CH. COFFIGNIER (*Bull. Soc. chim.*, 1906, [iii], **35**, 762—767).—Madagascar copal and the products obtained from it (1) by "running" by the usual pyrogenetic process and (2) by heating it at 260—290° in closed vessels with naphthalene by Terrisse's process (*Brev. français*, 334, 300, Oct. 1904) have been compared. The product obtained by "running" copal in the usual way is less soluble in alcohols, acetone, and amyl acetate, and more soluble in ether, turpentine oil, benzene, and chloroform than the crude copal. That prepared by Terrisse's process, when compared with the crude copal, is slightly less soluble in methyl alcohol, more soluble in chloroform, ether, turpentine oil, and benzene, whilst the solubility in ethyl alcohol and acetone remains practically unchanged.

Both products show a higher specific gravity, a lower melting point, a lower acid number, and a lower Köttstorfer number than the raw copal. There is no loss of weight when Terrisse's process is used and the product is lighter in colour than that obtained by the usual method. T. A. H.

American Colophony. PAUL LEVY (*Ber.*, 1906, **39**, 3043—3046).—The abietic acid, $C_{19}H_{29}\cdot CO_2H$, obtained by the author from American colophony, although identical crystallographically with the acid prepared by other workers, differs from this in melting point and in its capacity for crystallising. American colophony, on distillation under reduced pressure, yields an oily hydrocarbon, $C_{19}H_{30}$, which, after purification, boils at 210—211° under 26·5 mm. pressure, and has a sp. gr. 0·977 at 20°. This substance is readily soluble in ether and benzene, and is not very miscible with alcohol.

The foregoing hydrocarbon is undoubtedly identical with Deville, and Bischoff and Nastvogel's "colophene," and with Easterfield and Bagley's "abietene" (compare Trans., 1904, **85**, 1238).

Abietic acid, when treated with phosphorus pentachloride or thionyl chloride, furnishes an acid chloride, which, however, was not isolated in a state of purity, since it decomposes on distillation under reduced pressure. By repeated fractionation, an oily fluorescent hydrocarbon was obtained from the products of this decomposition, which boiled at 200—202° under 17 mm. pressure. To this substance, which is formed in accordance with the following equation, $C_{19}H_{29}\cdot COCl = C_{19}H_{28} + CO + HCl$, the author gives the name abietin. Towards organic solvents it behaves like abietene, and appears to correspond with the substance obtained by Kraemer and Spilker by the dry distillation of colophony (compare Abstr., 1900, i, 150). G. T. M.

The Identity of Thudichum's Phrenosin and Thierfelder's Cerebron. William J. Gies (*J. Biol. Chem.*, 1906, **2**, 159—182).—Thierfelder does not admit the identity of these two substances, although he admits on precisely the same grounds the identity of his cerebron with Gamgee's pseudo-cerebrin. The present paper is partly an historical literary retrospect into the subject, and is largely polemical. The identity of the two materials is maintained, as Gies and Posner originally stated. W. D. H.

Fern Secretions. I. Glandular Secretions of Gymnogramme chrysophylla and G. calomelanos. Wilhelm Zopf (*Chem. Centr.*, 1906, ii, 690—691; from *Ber. Deut. bot. Ges.*, **24**, 264—272).—From the extract obtained by momentary immersion of the fronds of *Gymnogramme chrysophylla* in ether, two substances have been isolated: a colourless, neutral wax, which melts at 63—64°, and *gynogrammen*, $C_{18}H_{18}O_5$, which crystallises in red, plate-like prisms, probably monoclinic, melts at 159°, and has an aromatic odour. It is insoluble in water, but dissolves readily in cold acetone and alcohol. It is decomposed by alkali solutions, gives a red colour with ferric chloride, and dissolves in concentrated sulphuric acid with an intense golden-yellow colour. On boiling with ethyl alcohol, it yields *gymnogrammidin*, which forms colourless needles melting at 114—115°.

From *Gymnogramme calomelanos*, a colourless substance, *calomelanen*, $C_{20}H_{22}O_6$, has been obtained; it has a camphoraceous odour, crystallises in small needles, melts at 141—142°, and dissolves readily in ethyl ether and ethyl alcohol. It gives a red colour with ferric chloride, and dissolves in concentrated sulphuric acid with a yellow colour. Boiling water decomposes it, and yields a volatile substance, which also has an odour resembling that of camphor. H. M. D.

Brazilin and Hæmatoxylin. Josef Herzig and Jacques Pollak (*Monatsh.*, 1906, **27**, 743—771. Compare Abstr., 1903, i, 270, 713; 1904, i, 81, 333; 1905, i, 605; this vol., i, 198).—The authors compare their structural formula for brazilin with that suggested by Pfeiffer (*Chem. Zeitschr.*, 1904, **3**, 390, 420) which closely resembles it.

When heated with acetic anhydride, sodium acetate, and zinc dust, the phenylhydrazine derivative of tetramethylhæmatoxylone forms a reduced *acetyl* derivative, $C_{24}H_{16}O_2N_2(OMe)_4$, which crystallises in white needles and melts at 188—192°.

[With Robert Fischer.]—The isomeride obtained from tetramethylhæmatoxylone is readily soluble in aqueous alkali hydroxides, and can be titrated sharply with phenolphthalein as indicator. When boiled with alcoholic potassium hydroxide or with alcoholic hydrogen chloride, it forms a *methyl ether*, $C_{16}H_7O_2(OMe)_5$, which crystallises from alcohol, melts at 99—102°, and when boiled with aqueous-alcoholic potassium hydroxide is hydrolysed, forming the isomeride of tetramethylhæmatoxylone melting at 169—171°. The methyl ether remains unchanged when boiled with acetic anhydride and sodium acetate; in alcoholic solution, it forms with concentrated sulphuric acid a red ring which disappears on shaking, but if sufficient acid is added the whole mixture becomes red, and the methyl ether is converted into β-dehydrotetramethylhæmatoxylin. The isomeride melting at 169—171° does not react with hydroxylamine or with phenylhydrazine, and is not reduced by zinc dust in boiling glacial acetic acid solution.

[With WOLFGANG KLUGER.]—Acetyltrimethylbrazilin has $[\alpha]_D$ +128°14′ at 20° or +125°54′50″ at 22°. Acetyltetramethylhæmatoxylin has $[\alpha]_D$ +151°28′32″ to +152°11′54″ at 20°. As tetra-acetylbrazilin prepared by acetylation of brazilin has $[\alpha]_D$ +76°24′31″, and that prepared by simultaneous reduction and acetylation of brazilein has $[\alpha]_D$ +75°26′30″, von Kostanecki and Feuerstein's formulæ for brazilin, which has one, and for brazilein, which has no asymmetric carbon atom, are probably incorrect. Almost all reactions of brazilin or its alkyl derivatives lead directly to the formation of inactive substances.

The triacetyl compound, $C_{16}H_9O(OAc)_3$ (Abstr., 1902, i, 482), and tetra-acetyl compound, $C_{16}H_8(OAc)_4$ (Abstr., 1901, i, 478), obtained by simultaneous reduction and acetylation of brazilin, have $[\alpha]_D$ −30′14″ and +3°22′46″ respectively.

Two preparations of trimethylbrazilone obtained by oxidation of trimethylbrazilin with chromic acid in acetic acid solution have $[\alpha]_D$ +1°34′4″ and −1°10′33″ respectively. Brazilinic acid has $[\alpha]_D$ +13′53″.

The formation of γ-tetramethyldehydrobrazilin by heating trimethylbrazilone with methyl iodide and potassium hydroxide on the water-bath is confirmed (compare Abstr., 1902, i, 482; 1904, i, 908).

[With ADOLF MAYRHOFER.]—The action of diacetylorthonitric acid (Pictet and Genequand, Abstr., 1902, i, 584) on ψ-trimethylbrazilone (the isomeride obtained by the action of sulphuric acid on trimethylbrazilone) in cooled glacial acetic acid solution leads to the formation of *nitro-ψ-trimethylbrazilone*, $C_{16}H_8O_3(OMe)_3\cdot NO_2$, which separates from ethyl acetate in yellowish-brown crystals, melts at 210—214°, is sensitive to light, and when boiled with acetic anhydride and sodium acetate yields a *product*, probably *nitro-β-acetyltrimethyldehydrobrazilin*, $C_{18}H_8O_3(OMe)_3\cdot NO_2$, forming glistening, yellow crystals and not melting at 260°.

When nitrated in the same manner, the monomethyl ether of ψ-trimethylbrazilone yields the *nitro*-derivative, $C_{16}H_7O_2(OMe)_4\cdot NO_2$, which crystallises from alcohol, melts at 196—198°, and does not react with diazomethane.

When treated with twice its weight of diacetylorthonitric acid in 10 vols. of glacial acetic acid, ψ-tetramethylhæmatoxylone (the isomeride of tetramethylhæmatoxylone) yields a mononitro-derivative, $C_{16}H_7O_3(OMe)_4\cdot NO_2$, which crystallises in long, glistening, yellow needles and melts at 221—222°. On acetylation this yields a *dehydroacetate*, $C_{18}H_7O_3(OMe)_4\cdot NO_2$, which crystallises in long, sulphur-yellow needles and melts at 198—200°, together with a small amount of a sparingly soluble *isomeride*, which crystallises in slender, light yellow needles, melts and decomposes at 289—291°, has a low specific gravity, and is formed on treatment of the product melting at 198—200° with acetic anhydride and sulphuric acid.

Nitration of ψ-tetramethylhæmatoxylone with four times its weight of diacetylorthonitric acid in four vols. of cooled glacial acetic acid leads to the formation of the *dinitro*-derivative, $C_{16}H_6O_3(OMe)_1(NO_2)_2$, which forms yellow crystals, melts and decomposes at 173—176°, and yields a *dehydroacetyl* derivative, $C_{18}H_6O_3(OMe)_4(NO_2)_2$; this crystallises in slender, yellow needles and melts and decomposes at 266—268°.

Nitration of the methyl ether of ψ-tetramethylhaematoxylone by means of diacetylorthonitric acid, leads to the formation of three isomeric *mononitro*-derivatives, $C_{16}H_6O_2(OMe)_5 \cdot NO_2$; the isomeride melting at 131—136° forms slender, yellow crystals and is prepared also by the action of diazomethane on nitro-ψ-tetramethylhaematoxylone; the second melts at 162—165° and forms short, slender, yellow needles, whilst that melting at 206—207° crystallises in long, slender, yellow needles. G. Y.

Yellow Colouring Matter in Surinam Greenheart. W. H. Bloemendal (*Chem. Centr.*, 1906, ii, 527; from *Pharm. Weekblad*, 1906, **43**, 678—686).—In the author's opinion, the dyes variously described as Tecomin, Grönhartin, Bethabarra colouring matter, Taigu-Lapachoic acid, and Lapachol are all identical with the yellow, crystalline substance of the formula $C_{15}H_{14}O_3$, obtained from the wood of the *Bignonia* and described first by Paterno and later by Hooker (Trans., 1896, **69**, 1355). P. H.

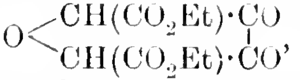
Colouring Matters of Phæophyceæ. M. Tswett (*Chem. Centr.*, 1906, ii, 529—530; from *Ber. Deut. bot. Ges.*, 1906, **24**, 235—244).—The production of the brown substance, phycophæin, is attributed to the oxidation of colourless chromogen. The following properties are mentioned as characteristic of carotin; unlike the xanthophylls or fucoxanthin it is more soluble in light petroleum, benzene, or carbon disulphide than in strong alcohol and is not adsorbed from a light petroleum solution by powdered calcium carbonate; moreover, neither the crystallised substance nor an alcoholic solution is turned blue by hydrochloric acid, and a solution in light petroleum shows three absorption bands, two at 492—475 $\mu\mu$ and one at 460—445 $\mu\mu$. In addition to carotin and fucoxanthin, the author has isolated from fucus extract a substance, *fucoxanthophyll*, which closely resembles fucoxanthin in its solubilities and its spectroscopic behaviour, but optical properties of which remain unchanged by treatment with sodium hydroxide. Chlorophyllin γ, which is also contained in the seaweed, is insoluble in light petroleum, but is soluble in alcohol or ether; when dissolved in the latter solvent, it shows absorption bands at 638—622 $\mu\mu$, 588—575 $\mu\mu$, and 465—440 $\mu\mu$. The natural brownish-green colour of algæ is produced as a result of the mixture of all the above-mentioned colouring matters. The destruction of the fucoxanthin is the cause of algæ turning green. P. H.

[Action of Formaldehyde on Gallocyanin]. Farbwerke vorm. L. Durand, Huguenin & Co. (D.R.-P. 171459).—Gallocyanin and formaldehyde condense to form a new colouring matter which is readily reduced with reducing agents such as zinc dust and hydrochloric acid, sodium hyposulphite or sodium sulphide to form a new leuco-base, which is obtained in the form of grey or yellow hydrochloride. This salt dissolves in water to a brownish-yellow solution; in concentrated sulphuric acid, it exhibits a blue-reddish-yellow dichroism. The leuco-base is precipitated by alkalis as a greenish-yellow, flocculent precipitate, which oxidises on exposure to air. The addition of manganese dioxide to an acid solution of the leuco-base develops an intense greenish-blue coloration. The leuco-base dyes wool in an acid bath. G. T. M.

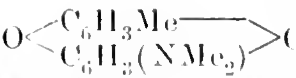
Conjugated Dionium Ring Systems. HERMAN DECKER (*Ber.*, 1906, **39**, 3069—3071. Compare Abstr., 1905, i, 667).—Attention is called to the facility with which certain cyclic complexes of high molecular weight undergo a reversible process of oxidation and reduction. Dinaphthylene dioxide dissolves in concentrated sulphuric acid to a light yellow solution in the absence of oxygen. In the presence of this or other oxidising agent, the colour changes to dark blue, due to the dioxonium salt (compare Bünzly and Decker, Abstr., 1905, i, 884). A small quantity of water added to the yellow solution precipitates the original compound, but larger quantities can be added to the blue solution, changing its colour first to red (carbinolmonoxonium salt), and then precipitating the yellow dicarbinol base. The blue solution is readily changed by reducing agents to the yellow, fluorescent solution of dinaphthylene dioxide.

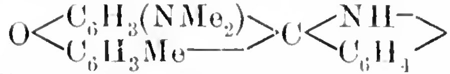
Similar relations have been observed between isologous coeroxene and between coerthiene derivatives (compare this vol., i, 687).

C. S.

Researches on Furans. 2 : 5-Dicarbethoxy-3 : 4-diketotetrahydrofuran. I. TREAT B. JOHNSON and CARL O. JOHNS (*Amer. Chem. J.*, 1906, **36**, 290—294).—*Ethyl* 3 : 4-*diketotetrahydrofuran*-2 : 5-*dicarboxylate*,  $O<\begin{matrix}CH(CO_2Et)\cdot CO\\ |\\ CH(CO_2Et)\cdot CO\end{matrix}$, obtained in quantitative yield by the condensation of ethyl oxalate with ethyl diglycollate, forms stout, prismatic crystals, melts at 189°, and is very soluble in hot alcohol; the *sodium* salt is obtained as a white powder. E. G.

Rhodamines. II. EMILIO NOELTING and KARL DZIEWOŃSKI (*Ber.*, 1906, **39**, 2744—2749. Compare Abstr., 1905, i, 935).—*Tetraethylrhodamine silver nitrate*, $C_{28}H_{30}O_3N_2,AgNO_3$, obtained by mixing alcoholic solutions of the components, crystallises in glistening, bluish-green plates. *apo*Rhodamine forms a similar compound which is decomposed when shaken with cold water.

The esters of aporhodamine are prepared readily by the usual catalytic method, using hydrogen chloride. *Ethyl*aporhodamine *hydrochloride*, $C_{25}H_{24}O_3NCl,5H_2O$, crystallises in pale red needles with a golden lustre, melts at 95°, and is not hydrolysed by boiling water. When decomposed by aqueous solutions of alkalis, the hydrochloride yields *apo*rhodamine, but with the theoretical amount of cold alcoholic potassium hydroxide, it yields the *carbinol ether* of the *ester*,  $O<\substack{C_6H_3Me——\\C_6H_3(NMe_2)}>C(OEt)\cdot C_6H_4\cdot CO_2Et$, in the form of colourless prisms melting at 105°. With hydrochloric acid, ethyl alcohol is eliminated and the hydrochloride of the ester regenerated.

apo*Rhodamine-imide*,  $O<\substack{C_6H_3(NMe_2)\\C_6H_3Me——}>C<\substack{NH-\\C_6H_4}>CO$, obtained by the action of hot alcoholic ammonia on the hydrochloride of the ester, crystallises in large, glistening prisms, melts at 227°, and contains a half molecule of alcohol of crystallisation. It dissolves in hot dilute acids, yielding colourless solutions. J. J. S.

Compounds of the Hydrochlorides of the Alkaloids with the Chlorides of the Heavy Metals and the Corresponding Bromine Compounds. A. Christensen (*J. pr. Chem.*, 1906, [ii], **74**, 161—187. Compare Classen and Zahorsky, Abstr., 1893, ii, 464; Wells, *ibid.*, 523; Goebbels, Abstr., 1895, i, 399).—Lead tetrachloride combines with quinine hydrochloride in hydrochloric acid solution to form an amorphous *additive* compound, which gradually becomes yellow and crystalline: with cinchonidine hydrochloride forming a yellow *precipitate* consisting of small prisms, and with cinchonine hydrochloride forming a *precipitate* consisting of rosettes of microscopic, yellow needles. These three additive compounds readily decompose, yielding an odour of chlorine.

In the same manner, from α-cinchonidine dibromide hydrochloride there is formed the *compound* $C_{19}H_{22}ON_2Br_2,2HCl,PbCl_4,2H_2O$, which is obtained in yellow, microscopic prisms and does not decompose when dried. The precipitate formed from β-cinchonidine dibromide hydrochloride is amorphous. With α-cinchonine dibromide hydrochloride there is formed a yellow *precipitate*,

$$C_{19}H_{22}ON_2Br_2,2HCl,PbCl_4,2H_2O,$$

which consists of concentric aggregates of microscopic needles; the *precipitate* formed with β-cinchonine dibromide hydrochloride is yellow and amorphous.

The action of potassium bromide solution on the freshly-prepared double salt of α-cinchonidine dibromide hydrochloride and lead tetrachloride leads to the formation of a *product* which crystallises in quadratic, yellow leaflets or prisms, and when treated with water yields lead bromide. The *product* of the action of lead bromide and bromine on β-cinchonidine dibromide in hydrobromic acid solution behaves as a mixture of the compounds $C_{19}H_{22}ON_2Br_2,2HBr,PbBr_4$ and $C_{19}H_{22}ON_2Br_2,2HBr,Br_2$.

Double salts of manganese trichloride (compare Rice, Trans., 1898, **73**, 258; Meyer and Best, Abstr., 1900, ii, 77) were prepared by adding a solution of the alkaloid in glacial acetic acid solution to manganese dioxide stirred into glacial acetic acid, and adding the calculated amount of 40 per cent. hydrochloric acid or passing hydrogen chloride into the mixture. With α-cinchonidine dibromide hydrochloride there is formed the *compound*

$$C_{19}H_{22}ON_2Br_2,2HCl,MnCl_3,2H_2O,$$

which forms green, microscopic crystals, decomposes and becomes brown on addition of water, and reacts with potassium iodide and hydrochloric acid, yielding the periodide. The similarly-constituted *salt* with β-cinchonidine dibromide hydrochloride contains H_2O, is obtained as a light green powder consisting of concentric aggregates of small crystals, and when exposed to air decomposes rapidly losing chlorine. With α- and β-cinchonine dibromide there are formed green, amorphous, hygroscopic *precipitates*, which decompose, losing chlorine in a desiccator.

The following double salts are formed by addition of alkaloids to ferric chloride in hydrochloric acid solution (Borsbach, Abstr., 1890, 643). With quinine, the salt $C_{20}H_{24}O_2N_2,2HCl,FeCl_3,H_2O$, which is obtained as a yellow, crystalline powder consisting of microscopic, hexagonal prisms; with cinchonidine, the *compound* $C_{19}H_{22}ON_2,2HCl,FeCl_3,2H_2O$, which crystallises in microscopic, yellow prisms; with cinchonine, the *salt* $C_{19}H_{22}ON_2,2HCl,FeCl_3,H_2O$ (?), which separates in sheaves of microscopic, yellow, rectangular crystals; with α-cinchonidine dibromide, the *salt*

$$C_{19}H_{22}ON_2Br_2,2HCl,FeCl_3,2H_2O\ (?),$$

which crystallises in sheaves of long needles; with strychnine, the *salt* $C_{21}H_{22}O_2N_2,HCl,FeCl_3$, which forms a precipitate consisting of microscopic, yellowish-brown crystals; with brucine, the *salt*

$$C_{23}H_{26}O_4N_2,HCl,FeCl_3 2H_2O\ (?),$$

which forms a heavy, greyish-brown precipitate, gradually changing into spherical crystals; with cocaine, the *salt*

$$C_{17}H_{21}O_4N,HCl,FeCl_3,$$

which separates as a sulphur-yellow, micro-crystalline powder; with morphine, the *compound* $C_{17}H_{19}O_3N,HCl,FeCl_3,H_2O$, crystallising in sheaves of microscopic, brown needles, giving the characteristic blue coloration obtained on addition of ferric chloride to morphine, and decomposing with formation of morphine hydrochloride when recrystallised from hydrochloric acid; with caffeine, the *salt* $C_8H_{10}O_2N_4,HCl,FeCl_3,H_2O$, forming microscopic, hexagonal, short crystals; with pyridine, the *compound* $C_5H_5N,HCl,FeCl_3$, crystallising in yellow, pointed, tetragonal prisms; with quinoline, the *salt* $C_9H_7N,HCl,FeCl_3$, which crystallises in microscopic, long, pointed prisms and is readily soluble in water.

Similar double salts of the alkaloids are formed with ferric bromide and hydrobromic acid; these are less stable than the corresponding chlorine compounds and can be isolated in a state of purity only in exceptional cases. With cinchonidine, the *salt* $C_{19}H_{22}ON_2,2HBr,FeBr_3,2H_2O$ separates as an orange-red, crystalline precipitate; the cinchonine *salt* is thrown down as an amorphous precipitate, changing gradually into small, yellow prisms; the quinine *salt* is obtained as a red, amorphous precipitate; the caffeine *salt*, $C_8H_{10}O_2N_4,HBr,FeBr_3,H_2O$, forms a reddish-brown, microcrystalline powder; the quinoline *salt*, $C_9H_7N,HBr,FeBr_3$, separates in reddish-brown, microscopic, hexagonal crystals. G. Y.

Clavine, a New Constituent of Ergot. ERNST VAHLEN (*Chem. Centr.*, 1906, ii, 690; from *Arch. exper. Path. Pharm.*, **55**, 131—163).—*Clavine*, $C_{11}H_{22}O_4N_2$, is obtained when an aqueous extract of ergot is precipitated with a hot saturated solution of barium hydroxide, the barium removed from the solution by carbon dioxide, and the concentrated filtrate extracted with hot alcohol. It forms elongated needles or small, nacreous, rhombic plates and melts at 262—263° in a closed tube. When heated carefully it sublimes, forming star-shaped aggregates of small prisms. It dissolves readily in water and is not precipitated by alkali hydroxides or carbonates. It is only slightly soluble in ethyl alcohol, and insoluble in ether, ethyl acetate, or light petroleum.

In aqueous solution it is split up into two substances having approximately the same molecular weight. By addition of copper hydroxide or a solution of copper acetate, the copper salts of two acids, both containing nitrogen, are formed, one of which is soluble, the other insoluble in water.

The aqueous solution of clavine has an insipid taste and yields no precipitate with the alkaloid reagents. It is much more soluble in acid and alkaline solutions than in water. On evaporation of a hydrochloric acid solution, delicate prisms of the *hydrochloride*, $C_{11}H_{22}O_4N_2,2HCl$, are obtained. It exerts a specific action on the uterus causing this to contract.
H. M. D.

Morphine. VIII. Trihydroxyphenanthrene from Hydroxycodeine. LUDWIG KNORR and HEINRICH HÖRLEIN (*Ber.*, 1906, 39, 3252—3255).—The methoxydiacetoxyphenanthrene obtained from hydroxycodeine (compare Knorr and Schneider, this vol., i, 449) is oxidised by chromic and glacial acetic acids to Vongerichten's acetylmethylmorpholquinone (Abstr., 1898, i, 281). From this it follows that the hydroxyl group, introduced into codeine by oxidation, must be situated in position 9 or 10, and, moreover, that as this hydroxyl group exhibits an alcoholic and not a phenolic function, consequently the "bridge" carbon atoms of the phenanthrene nucleus, not only in codeine, but also in methylmorphimethine, must be dihydrogenated. This result renders untenable Freund's formulæ for thebaine and codeine (Abstr., 1905, i, 918; this vol., i, 303) and Pschorr's "pyridine" formula for morphine (Abstr., 1903, i, 193).

Methoxydiacetoxyphenanthrene has been obtained by Pschorr from dichloromethylmorphimethine (see following abstract). C. S.

Halogen Derivatives of Morphine and Codeine, and their Degradation. ROBERT PSCHORR (*Ber.*, 1906, 39, 3130—3139).—[With HERMANN VOGTHERR].—*Chloromorphide*, $C_{17}H_{18}O_2NCl$, resulting from the action of hydrogen chloride on morphine at the ordinary temperature, melts at 192° (corr.); the *methiodide*, $C_{17}H_{18}O_2NCl,MeI$, melts at 207° (corr.).

Bromomorphide hydrobromide, $C_{17}H_{18}O_2NBr,HBr$, obtained by treating morphine with phosphorus pentabromide and subsequently with hydrogen bromide, decomposes at 196°; the *base*, $C_{17}H_{18}O_2NBr$, forms needles and melts at 170°, the *methiodide* at 200°, and the *anilinocarboxylic ester*, $C_{24}H_{23}O_3N_2Br$, at 204°.

Bisthiomorphide, $(C_{17}H_{19}O_2NS)_2$, is prepared by heating chloro- or bromo-morphide with alcoholic potassium hydrosulphide; it melts at 201° and forms a *methiodide*, $(C_{19}H_{23}O_2NSI)_2$, which melts at 253° and is also obtained from *bisthiocodide*, $(C_{18}H_{20}O_2NS)_2$, which is soluble in alkali and melts at 200° (corr.). *Ethylthiocodide*, $C_{20}H_{25}O_2NS$, obtained by heating bromocodide with alcoholic sodium mercaptide in an atmosphere of hydrogen, melts at 145° (corr.).

[With E. Kuhtz and Heinrich Roth.]—*Chlorocodide methiodide*,

$$C_{19}H_{23}O_2NClI,$$

decomposes at 166—167° and does not yield chloromethylmorphimethine by heating with sodium hydroxide. The *hydrochloride* of the chlorinated methine base, $C_{19}H_{22}O_2NCl,HCl$, results, however, when α-methylmorphimethine is treated with phosphorous chloride in chloroform; it crystallises in tufts of needles and melts at 177—178° (corr.). The base has not been obtained crystalline; the *methiodide*,

$$C_{19}H_{22}O_2NCl,MeI,$$

forms slender needles and melts at 163° (corr.). In the absence of a solvent, the preceding reaction results in the formation of the *compound* $C_{19}H_{22}O_2N\cdot O\cdot P(OH)_2,HCl$.

By heating with acetic anhydride, chloromethylmorphimethine hydrochloride yields Knorr's acetylmethyldihydroxyphenanthrene (Abstr., 1889, 905). The nitrogenous fission product is, according to the conditions of the decomposition, either methyl-β-hydroxyethylamine or dimethyl-β-hydroxyethylamine and a base having the composition of tetramethylethylenediamine.

Dichloromethylmorphimethine, $C_{19}H_{23}O_3NCl_2$, obtained as the hydrochloride by the action of phosphoric chloride on α-methylmorphimethine in chloroform, decomposes at 180—181° and forms a crystalline *methiodide* which decomposes at 153—154°. The decomposition of the base by acetic anhydride yields the same basic products as the monochloro-compound, and 3-methoxy-4 : 9-(or 4 : 10)-diacetoxyphenanthrene. The latter substance, which has been obtained by Knorr by the degradation of hydroxycodeine, has its constitution partially determined by its oxidation to 4-acetoxy-3-methoxyphenanthraquinone.

Benzoylcodeine methiodide, $C_{26}H_{28}O_4NI$, melts at 254° (corr.). *Benzoyl-α-methylmorphimethine* melts at 182—183°, and its *methiodide*,

$$C_{27}H_{30}O_4NI,$$

at 188°. Codeine yields with phenylcarbimide the *anilinocarboxylic ester*, which melts at 141°; the *methiodide*, $C_{26}H_{29}O_4N_2I$, at 141°. The corresponding *compound* of α-methylmorphimethine melts at 122—123°, and its *methiodide* at 251° (corr.).

C. S.

Constitution of *apo*Morphine. Robert Pschorr [and Walther Karo] (*Ber.*, 1906, **39**, 3124—3128. Compare Abstr., 1903, i, 193).—The methylation of *apo*morphine by methyl sulphate instead of by diazomethane leads to the ultimate formation of dimethoxyvinylphenanthrene in quantitative yield. When the latter is oxidised rapidly in acetone by potassium permanganate, there is formed, in addition to the acid described previously (*loc. cit.*), *dimethoxyphenanthrylglycol*,

$$C_{14}H_7(OMe)_2\cdot CH(OH)\cdot CH_2\cdot OH,$$

which forms glistening leaflets and melts at 145° (corr.); the *acetate*, $C_{22}H_{22}O_6$, melts at 126—127° (corr.).

Pentabromodimethoxyvinylphenanthrene, $C_{18}H_{13}O_2Br_5$, resulting by the bromination of the tribromo-compound (*loc. cit.*), melts at 153—154° (corr.).

By distillation with zinc dust, dimethyl*apo*morphimethine or dimethoxyvinylphenanthrene yields two *ethylphenanthrenes*, α and β. The former is volatile with steam, melts at 109—110°, and forms a *picrate*, $C_{16}H_{14},C_6H_3O_7N_3$, which melts at 138—140° (corr.), and a *quinone* which melts at 187—188° (corr.).

The β-compound crystallises in needles and melts at 172—173° (corr.). The nitrogenous products of the distillation are hydrogen cyanide, ammonia, and trimethylamine. C. S.

Narceine. I. Alkylnarceines and Alkylhomonarceines.

Rudolph Tambach and Carl Jaeger (*Annalen*, 1906, **349**, 185—200. Compare Freund and Frankforter, Abstr., 1894, i, 58).—The sodium salt of narceine melts at 163—165°.

When boiled together in absolute alcoholic solution, narceine and methyl sulphate form an additive compound, which crystallises from alcohol in rhomboids or from water in slender needles, and melts at 200—201°.

Methylnarceine,

$$CO_2H\cdot C_6H_2(OMe)_2\cdot CO\cdot CHMe\cdot C_6H(CH_2\cdot CH_2\cdot NMe_2)(OMe){<}\substack{O\\O}{>}CH_2,$$

is formed by treating narceine with the calculated amounts of *N*-sodium hydroxide and methyl sulphate; it melts and decomposes at 266°; the *hydrochloride*, $C_{24}H_{29}O_8N,HCl$, crystallises from alcohol and melts at 243°; the *sodium* derivative crystallises in nacreous, glistening leaflets and is readily soluble in water or alcohol; the *platinichloride* forms yellow leaflets and melts at 209—210°.

Ethylnarceine, prepared by the action of ethyl sulphate on narceine in sodium hydroxide solution, melts at 175—177°; the *hydrochloride*, $C_{25}H_{31}O_8N,HCl$, melts at 231°; the *platinichloride* melts at 174°. When heated with alcoholic hydrogen chloride, the base forms *ethyl ethylnarceine*,

$$CO_2Et\cdot C_6H_2(OMe)_2\cdot CO\cdot CHEt\cdot C_6H(CH_2\cdot CH_2\cdot NMe_2)(OMe){<}\substack{O\\O}{>}CH_2,$$

which is isolated as the *hydrochloride*, $C_{27}H_{35}O_8N,HCl$, melting at 218·5—219°; the *platinichloride* melts at 220°.

The alkylnarceines may be prepared by the action of alkyl haloids instead of the alkyl sulphates on narceine in alcoholic sodium or potassium hydroxide instead of *N*-sodium hydroxide solution or on sodium narceine.

The alkali salts of narceine react with 2 mols. of methyl sulphate in alcoholic solution, forming an *additive* compound of methylnarceine and methyl sulphate,
$CO_2H\cdot C_6H_2(OMe)_2\cdot CO\cdot CHMe\cdot C_6H(C_2H_4\cdot NMe_3\cdot SO_4Me)(OMe)\vdots O_2\vdots CH_2$,
which is formed also by the action of methyl sulphate on methylnarceine in alcoholic solution; it melts at 184—186° and is soluble in alcohol.

The authors have repeated part of Freund's experiments (*loc. cit.*). The action of methyl iodide on narceine in boiling ethyl-alcoholic potassium hydroxide, or on sodium narceine in boiling methyl or ethyl alcohol, or on methylnarceine at 110—120°, leads to the formation of methylnarceinium methiodide melting at 207—209°. The action of ethyl iodide on sodium narceine in boiling ethyl-alcoholic solution or in the absence of a solvent, leads to the formation of ethylnarceinium ethiodide; methylnarceine was not obtained by the action of methyl alcohol on sodium narceine. The alcohol takes no part in the reaction.

Ethylnarceinium methiodide, formed by heating ethylnarceine with methyl iodide, melts at 209—211° or, when mixed with methyl narceinium methiodide, at 200°. *Ethyl narceinium ethiodide*, prepared from ethylnarceine and ethyl iodide, crystallises in sheaves of large needles, melts at 191—193°, and forms a yellow precipitate when treated with sodium hydroxide in aqueous solution.

Methylhomonarceine, prepared by treating homonarceine with methyl sulphate and sodium hydroxide, is isolated as the *hydrochloride*, which crystallises in sheaves of prisms and melts and decomposes at 230—231°; the *platinichloride* melts at 181—182°.

Ethyl methylhomonarceine hydrochloride, prepared by boiling the preceding substance with alcoholic hydrogen chloride, melts at 212°, and gives an intense yellow coloration with aqueous sodium hydroxide; the platinichloride melts at 217—218°.

Ethylhomonarceine, prepared from homonarceine, ethyl sulphate, and *N*-sodium hydroxide, is isolated as the *hydrochloride*, melting and decomposing at 212°; the platinichloride melts at 152—155°.

*apo*Narceine,

$$\mathrm{C_6H_2(OMe)_2}<\genfrac{}{}{0pt}{}{\mathrm{CO}}{\mathrm{CO}}>\mathrm{CH\cdot C_6H(CH_2\cdot CH_2\cdot NMe_2)\,(OMe)}<\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{O}}>\mathrm{CH_2},$$

is prepared by heating narceine with phosphorus oxychloride; it crystallises from alcohol, melts at 112—115°, is readily soluble in hot alcohol, but only sparingly so in water, and is insoluble in aqueous alkali hydroxides. The *hydrochloride*, $C_{23}H_{25}O_7N,HCl,H_2O$, is an intense canary-yellow, melts at 144°, and is hydrolysed by boiling aqueous sodium hydroxide. G. Y.

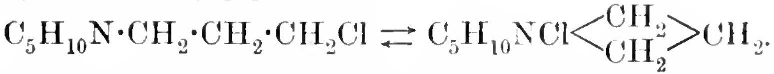
Constitution of Histidine. ADOLF WINDAUS and FRANZ KNOOP (*Beitr. chem. Physiol. Path.*, 1906, **8**, 406—408. Compare Abstr., 1905, i, 834).—According to Niementowski (*Ber.*, 1899, **32**, 1460; compare O. Fischer, Abstr., 1901, i, 413), the rupture of an iminazole ring by the action of benzoyl chloride is by no means general, and hence Fränkel's criticism (this vol., i, 547) of the authors' iminazole formula for histidine has little value.

Potassium hydroxide and benzenesulphonic chloride, or naphthalene sulphonic chloride, do not rupture the ring in methyliminazole. The histidinecarboxylic acid described by Fränkel melts at 209° (corr.), and not at 195°, and is identical with the glyoxaline-4-carboxylic acid previously described by the authors. J. J. S.

Erlenmeyer, jun.'s, Brucine Cinnamates. WILLY MARCKWALD and RICHARD METH (*Ber.*, 1906, **39**, 2598—2600. Compare Erlenmeyer, jun., Abstr., 1905, i, 892; this vol., i, 21, 176; Erlenmeyer, jun., and Barkow, this vol., i, 429; Marckwald and Meth, this vol., i, 360, 585).—The authors consider that Erlenmeyer, jun.'s, conclusions regarding the stereoisomeric cinnamic acids are erroneous. The optically inactive salt, described by Erlenmeyer as having been obtained from naturally occurring cinnamic acid and brucine, and sometimes also from the synthetical acid and brucine, is obtained by the authors by the combination of cinnamic acid (2 mols.) and brucine (1 mol.). The *salt* $C_{23}H_{26}O_4N_2,(C_9H_8O_2)_2$ melts at 135°, as Erlenmeyer found, but is not quite inactive, a 1 per cent. solution of it giving $\alpha_D - 5'$ in a 2-dcm. tube. A. McK.

Preparation of Sodium Theobromine Formate. F. Hoffmann, La Roche & Cie. (D.R.-P., 172932).—The double salt, *sodium theobromine formate*, $NaC_7H_7O_2N_4,HCO_2Na,H_2O$, is prepared by mixing aqueous solutions containing molecular proportions of pure sodium theobromine and anhydrous sodium formate; the solution is evaporated to dryness on the water-bath, when the product is obtained as a white powder of bitter taste. This substance is employed therapeutically, and has a powerful diuretic action. G. T. M.

Tertiary and Quaternary Bases from Piperidine. Siegmund Gabriel and James Colman (*Ber.*, 1906, 39, 2875—2888. Compare Gabriel and Stelzner, Abstr., 1896, i, 702; Hörlein and Kneisel, this vol., i, 458).—γ-Chloropropylpiperidine is transformed into a quaternary salt when evaporated with water, but if the heating is continued in order to drive off all the water, the quaternary salt is transformed back into γ-chloropropylpiperidine,



$$C_5H_{10}N\cdot CH_2\cdot CH_2\cdot CH_2Cl \rightleftarrows C_5H_{10}NCl{<}{\begin{matrix}CH_2\\CH_2\end{matrix}}{>}CH_2.$$

When the pure quaternary salt is distilled with 50 per cent. potassium hydroxide solution until the distillate is no longer alkaline, the chief product is a *base*, $C_{16}H_{32}ON_2$, distilling at 336—339°. No neutral products and no piperidine, allylpiperidine, or trimethylenedipiperidine appear to be formed. These products could not be isolated when the crude chloride containing unaltered γ-chloropropylpiperidine was used.

The base $C_{16}H_{32}ON_2$ yields an *aurichloride* melting at 131—132°, a *platinichloride*, $C_{16}H_{34}ON_2PtCl_6$, which sinters at 220°, and melts and decomposes at 223—224°, a *picrate* melting at 150—151°, a *hydrochloride* in the form of a crystalline, hygroscopic powder melting at 220—221°, and a *hydriodide* in colourless rhombs melting at 135—136°. The same base is obtained when trimethylenepiperylium hydroxide is heated with water at 50°; it is represented as *dipiperidinodipropyl ether*,

$$O(CH_2\cdot CH_2\cdot CH_2\cdot NC_5H_{10})_2.$$

The base reacts with methyl iodide, yielding a *dimethiodide*,

$$C_{16}H_{32}ON_2,2CH_3I,$$

which melts at 165—168° after sintering at 140°. The corresponding *platinichloride*, $C_{18}H_{38}ON_2PtCl_6$, melts and decomposes at 244°, and the *aurichloride* melts at 164—165° after sintering at 155°. When heated with hydrochloric acid at 150°, the base yields γ-chloropropylpiperidine hydrochloride, and when boiled with hydriodic acid γ-iodopropylpiperidine hydriodide. The *picrate* of γ-iodopropylpiperidine sinters at 95° and melts at 99—100°.

γ-*Methoxypropylpiperidine*, $C_5H_{10}N\cdot CH_2\cdot CH_2\cdot CH_2\cdot OMe$, obtained by the action of α-chloropropyl methyl ether on piperidine, is an oil distilling at 199—203° under 766 mm. pressure. It dissolves readily in water, and the solution has a distinctly alkaline reaction. The *aurichloride* crystallises in golden-yellow, hexagonal plates, melting at 68—69°. When boiled for a short time with hydriodic acid, the base yields γ-iodopropylpiperidine hydriodide.

Trimethylenedipiperidine and trimethylene bromide were condensed in the hope of obtaining the bromide of the octocyclic base described by Hörlein and Kneisel, but without result. J. J. S.

Reduction of *o-p*-**Dinitrophenylpiperidine.** LEOPOLD SPIEGEL and A. UTERMANN (*Ber.*, 1906, **39**, 2631—2638).—Since substances of the aminophenylpiperidine class are of pharmacological interest, the authors describe several new compounds prepared from *o-p*-dinitrophenylpiperidine by a modification of Lellmann and Geller's method (Abstr., 1888, 1107). Whilst Lellmann and Geller obtained from the dinitro-compound in question substances containing chlorine, the authors by variation of the conditions obtain *o-p*-diaminophenylpiperidine and also *o*-amino-*p*-nitrophenylpiperidine. The position of the nitro-group in the latter substance was determined by transformation into *p*-nitrophenylpiperidine by means of the diazo-reaction. By the reduction of the dinitro-compound in alcoholic solution with ammonium sulphide, a small amount of *p* amino-*o*-nitrophenylpiperidine was also obtained.

o-p Dinitrophenylpiperidine was prepared by adding piperidine (2 mols.) to an alkaline solution of chloro-2 : 4-dinitrobenzene, keeping the temperature below 45°, and then boiling until the solution was complete.

o-p-*Diaminophenylpiperidine*, $C_5H_{10}N,C_6H_3(NH_2)_2$, prepared by the reduction of *o-p*-dinitrophenylpiperidine by stannous chloride, separates from light petroleum in prisms and melts at 76°. Its *hydrochloride* forms transparent needles and melts indefinitely at 225°.

Diacetyl-o-p-*diaminophenylpiperidine hydrochloride* separates from a mixture of alcohol and ether in needles and melts at 245°. *Diacetyl*-o-p-*diaminophenylpiperidine* separates from alcohol or light petroleum in grey leaflets and melts at 183°.

Piperidino-m-*phenylenediurethane*, $C_5H_{10}N\cdot C_6H_3(NH\cdot CO_2Et)_2$, prepared by the addition of ethyl chlorocarbonate to an ethereal solution of *o-p*-diaminophenylpiperidine, separates from a mixture of acetone and light petroleum in transparent, rhombic plates.

Piperidino m-*phenylenedicarbamide*, $C_5H_{10}N\cdot C_6H_3(NH\cdot CO\cdot NH_2)_2$, prepared from potassium *iso*cyanate and *o-p*-diaminophenylpiperidine hydrochloride, separates from a mixture of acetone and light petroleum in stellate needles and melts at 190°.

p-*Nitro* o-*aminophenylpiperidine*, $C_5H_{10}N\cdot C_6H_3(NO_2)\cdot NH_2$, prepared by the partial reduction of *o-p*-dinitrophenylpiperidine by ammonium sulphide or by stannous chloride, separates from light petroleum in prisms or pyramids and melts at 86°. Its *hydrochloride* is unstable.

4-*Nitro-2-acetylaminophenylpiperidine*, $C_5H_{10}N\cdot C_6H_3(NO_2)\cdot NHAc$, separates from light petroleum in yellow prisms and melts at 106°.

Piperidino-4-nitrophenyl-2-urethane, $C_5H_{10}N\cdot C_6H_3(NO_2)\cdot NH\cdot CO_2Et$, separates from a mixture of acetone and water in pale yellow needles and melts at 120°.

Dipiperidino-4-nitrophenyl-2-carbamide, $CO[NH\cdot C_6H_3(NO_2)\cdot C_5H_{10}N]_2$, prepared by the addition of a solution of phosgene in toluene to a solution of 4-nitro-2-aminophenylpiperidine in benzene, separates from a mixture of acetone and light petroleum in needles and melts at 206°.

2-*Nitro-4-aminophenylpiperidine*, $C_5H_{10}N\cdot C_6H_3(NO_2)\cdot NH_2$, formed, together with its isomeride, by the reduction of 2 : 4-dinitrophenylpiperidine with ammonium sulphide, separates from light petroleum in dark red needles and melts at 112·5°. A. McK.

isoPropyl-4-stilbazole, *m*-Methyl-4-stilbazole, and *m*-Methyl-2-stilbazole. HERMANN FREUND (*Ber.*, 1906, 39, 2833—2837).—iso*Propyl-4-stilbazole*, prepared by heating 4-picoline with cuminaldehyde in presence of zinc chloride, melts at 65—67° and forms a golden-yellow, crystalline *picrate* melting at 188—190°, a yellowish-white *mercurichloride* melting at 165—167°, and a yellow *platinichloride* melting at 191—193°. The *dibromide* forms reddish-yellow crystals, which sinter at 135° and melt at 144—146°. iso*Propyldihydro-4-stilbazole* is a yellow oil boiling at 185—195° under 35 mm. pressure; the *aurichloride* melts at 116—117°.

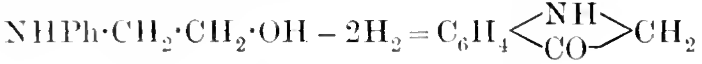
m-*Methyl-4-stilbazole* is a colourless oil distilling between 220° and 225° under 35 mm. pressure; the *picrate* forms yellow crystals, melting at 194—196°; the *aurichloride* sinters at 158° and melts at 166—168°; the *platinichloride* melts between 194° and 195°, and the *dibromide* at 125—127°. m-*Methyldihydro-4-stilbazole* is a colourless liquid, boiling at 220° under 60 mm. pressure; the *picrate* melts at 122—124°, the *platinichloride* at 171—172°. m-*Methyl-4-stilbazoline* is a viscous, reddish-yellow oil, distilling at 200° under 50 mm. pressure.

m-*Methyl-2-stilbazole* is a light, mobile oil, boiling at 220° under 45 mm. pressure; the *picrate* melts at 214—215°; the *aurichloride* forms needles melting at 135—136°; the *platinichloride* melts at 186—187°; the *dibromide* melts at 145—146°. m-*Methyldihydro-2-stilbazole* is a colourless oil, boiling at 220° under 35 mm. pressure; the *picrate* melts at 131—132°, the *aurichloride* at 79—80°, and the *platinichloride* at 156—157°. m-*Methyl-2-stilbazoline* is a light oil, distilling at 195—197° under 35 mm. pressure. E. F. A.

Preparation of Indoxyl and its Derivatives. BADISCHE ANILIN- UND SODA-FABRIK (D.R.-P. 171172).—α-Hydroxyethylaniline,

$$NHPh\cdot CH_2\cdot CH_2\cdot OH,$$

its homologues, alkali derivatives, carboxylic acids, or the *N*-alkyl derivatives of the foregoing substances when fused with alkali metals, alkali amides, alkali hydroxides, or mixtures of these with the oxides of the alkaline earth metals, furnish indoxyl and indigotin on appropriate treatment:



$$NHPh\cdot CH_2\cdot CH_2\cdot OH - 2H_2 = C_6H_4\Big<\begin{matrix}NH\\CO\end{matrix}\Big>CH_2$$

$$\text{or } C_6H_4\Big<\begin{matrix}NH-\\C(OH)\end{matrix}\Big>CH.$$

G. T. M.

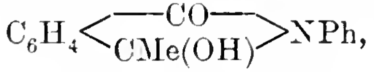
A New Indolenine Base. Dušan J. Grgin (*Monatsh.*, 1906, **27**, 731—742. Compare Plancher, Abstr., 1898, i, 536; Brunner, Abstr., 1900, i, 360).—*p*-Tolylhydrazine reacts with *iso*butaldehyde at 60°, forming water and 3 : 3 : 5-*trimethylindolenine*, which is isolated as the *zincochloride*, $(C_{11}H_{13}N)_2ZnCl_2$; this crystallises from alcohol in almost white leaflets and melts at 208—209°. The *base*, $C_6H_3Me\Big<\begin{matrix}CMe_2\\N\end{matrix}\Big>CH$, boils at 198—200° under 30 mm. pressure, crystallises with difficulty in almost colourless leaflets, melts at 142—143°, or, in consequence of polymerisation, after four and a half days in a vacuum at 156—157°, or after twenty days at 172—173°. The base melting at 172—173° forms with silver nitrate a *precipitate*, $(C_{11}H_{13}N)_2,C_{11}H_{12}NAg$, which is sensitive to light; the base melting at 142—143° does not form a precipitate with silver nitrate. The *picrate*, $C_{11}H_{13}N,C_6H_3O_7N_3$, crystallises in glistening, yellow prisms and melts at 169—170°; the *platinichloride*, $(C_{11}H_{13}N)_2H_2PtCl_6$, crystallises in dark yellow prisms.

When heated with concentrated hydrochloric acid in a reflux apparatus, the indolenine base is converted into 2 : 3 : 5-trimethyl indole, which melts at 190° and forms a picrate melting at 177—180° (compare Wolff, Abstr., 1889, 259).

Digestion of the indolenine base with ammoniacal silver nitrate on the water-bath leads to the formation of the corresponding *indolinone*, which is obtained as a white, crystalline substance, becoming brown on drying, and melting at 146°.

The action of bromine on the indolenine base in hydrochloric acid solution leads to the formation of the *derivative*, $C_{11}H_{12}ONBr$, which crystallises in light yellow leaflets and melts at 203—204°. G. Y.

Action of Mixed Organomagnesium Compounds on Imides. Constantin Béis (*Compt. rend.*, 1906, **143**, 430—432. Compare Abstr., 1904, i, 503, 671; Sachs and Ludwig, Abstr., 1904, i, 266).—Phenylphthalimide reacts with nascent magnesium alkyl halides to form substituted *iso*indolinones, and the following compounds were thus prepared. 3-*Hydroxy*-2-*phenyl*-3-*methyl*isoindolinone,



$$C_6H_4\Big<\begin{matrix}CO\\CMe(OH)\end{matrix}\Big>NPh,$$

forms colourless crystals melting at 185°, and 3-*hydroxy*-2-*phenyl*-3-*ethyl*iso*indolinone*, $C_6H_4\Big<\begin{matrix}CO\\CEt(OH)\end{matrix}\Big>NPh$, colourless crystals melting at 160°. With nascent magnesium phenyl bromide, phenylphthalimide yields a mixture of 3-*hydroxy*-2 : 3-*diphenyl*iso*indolinone*, melting at 195°, and benzoylbenzophenone, $C_6H_4(COPh)_2$, melting at 149° (compare Zincke, this Journal, 1876, i, 703), separated by their difference of solubility in benzene and in alcohol. M. A. W.

Halogen Derivatives of 8-Methylquinoline and Nitro-8-quinolinealdehyde. JOH. HOWITZ and PAUL NÖTHER (*Ber.*, 1906, **39**, 2705—2713. Compare Abstr., 1902, i, 397; 1905, i, 471).—The compounds described previously as 8-bromomethylquinoline and 3-bromo-8-bromomethylquinoline are in reality 8-chloromethylquinoline and 3-bromo-8-chloromethylquinoline respectively, since in the course of their preparation hydrochloric acid is employed, whereby the bromine in the side-chain is replaced almost entirely by chlorine. Pure 8-chloromethylquinoline crystallises in large, glistening plates and melts at 56°.

When the product obtained under Lang's conditions (*Diss.*, Freiburg, 1898) is dissolved in a mixture of equal volumes of concentrated sulphuric acid and water, and the solution poured into a large volume of water, 3-*bromo*-8-*bromomethylquinoline* is precipitated, whilst from the filtrate sodium hydroxide precipitates 8-*bromomethylquinoline*. The former, $C_9NH_5Br{\cdot}CH_2Br$, separates from alcohol in colourless leaflets and melts at 145°. The latter, $C_9NH_6{\cdot}CH_2Br$, separates from light petroleum in long, colourless needles or prisms, melts at 84°, and forms a *hydrobromide*, $C_9NH_6{\cdot}CH_2Br,HBr$, which darkens at 250°, but does not melt at 320°. By nitration it yields 5-*nitro*-8-*bromomethylquinoline*, $NO_2{\cdot}C_9NH_5{\cdot}CH_2Br$, which forms yellow needles or prisms and melts at 116°.

5-*Nitro*-8-*iodomethylquinoline*, $NO_2{\cdot}C_9NH_5{\cdot}CH_2I$, obtained from the corresponding chloro-compound and potassium iodide in aqueous-alcoholic solution, forms yellow needles and melts at 142°. By oxidation with dilute nitric acid (1 : 1), a quantitative yield of 5-*nitro*-8-*quinolinealdehyde*, $NO_2{\cdot}C_9NH_5{\cdot}CHO$, is obtained, which separates from hot water in slender, white needles, melts at 146—147°, reduces ammoniacal silver solutions, and is oxidised by chromic acid in warm dilute sulphuric acid to 5-*nitro*-8-*quinolinecarboxylic acid*,

$$NO_2{\cdot}C_9NH_5{\cdot}CO_2H,$$

which melts at 212°. C. S.

[Action of Alkyl Sulphates and Sulphonates on Quinoline Bases.] FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 170048, 170049).—The colouring matters produced by the interaction of alkylsulphonates and quinoline bases, and subsequent treatment with alkali hydroxides, are valuable sensitising compounds which are readily prepared and have favourable absorption spectra.

Quinaldine and ethyl ethanesulphonate combine additively to form an oily product which on treatment with alcoholic potash furnishes a colouring matter crystallising from ether or alcohol in green bronzy needles, and dissolving in water to a red solution.

The additive product, $C_{10}NH_9Et{\cdot}SO_3Ph$, of quinaldine and ethyl benzenesulphonate was obtained crystalline and melted at 105°; when treated with warm alcoholic potash it furnished a colouring matter separating in bright golden-bronzy leaflets. A similar compound was produced from quinaldine and ethyl *p*-bromotoluenesulphonate. The additive compounds obtained from ethyl *p*-toluenesulphonate and 2 : 6-dimethylquinoline and quinaldine melted at 120° and 134° respectively;

that from this ester and 6-bromoquinoline was oily, but all gave colouring matters on treatment with alcoholic potash.

2 : 7- and 2 : 6-Dimethylquinolines combine additively with methyl sulphate, and in the latter case a crystalline product melting at 212° was obtained. On treatment with alcoholic potash, crystalline colouring matters are produced, the compound from the 2 : 7-base having a steel-blue lustre, whilst that from the 2 : 6-isomeride separates in lustrous, dark green needles. G. T. M.

Colouring Matters of the Quinolinium Series. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 172118).—By the action of alkalis on the alkyl halides of quinaldine bases, or mixtures of these salts of the quinaldine and quinoline bases, red colouring matters are produced which have been employed as sensitisers in photographic practice. It is now found that quite different products are obtained when the alkali acts on these bases in the presence either of formaldehyde or of substances yielding this aldehyde. A colouring matter dissolving readily in the organic solvents, and sparingly in water to intense blue solutions, is produced on treating an alcoholic solution of quinoline and quinaldine hydriodides with sodium hydroxide and formaldehyde. The new compound separates in well-defined crystals having a green metallic reflex ; it can be recrystallised from boiling methyl alcohol. Similar colouring matters are obtained from the methochlorides of quinoline and quinaldine, and the reaction takes place also in aqueous or pyridine solutions. G. T. M.

Dyeing Properties of the Condensation Products of Quinaldine with Aldehydes. Emilio Noelting and E. Witte (*Ber.*, 1906, **39**, 2749—2751).—Benzylidenequinaldine [2-styrylquinoline] (Abstr., 1884, 336) itself is a dye, and a 3 per cent. solution of the hydrochloride yields an intense yellow colour with cotton mordanted with tannic acid. The *p*-nitro-derivative (Bulach, Abstr., 1887, 976) gives a somewhat more greenish shade. The isomeric *o*- and *m*-nitro-compounds, piperonylidene- and nitropiperonylidene-quinaldine, give yellow shades. Dihydroxybenzylidenequinaldine (Nencki, Abstr., 1894, i, 520), in the form of its hydrochloride, dyes wool, silk, or cotton mordanted with tannic acid orange-red. The *diacetyl* derivative, which melts at 165°, gives a yellow shade.

p-*Dimethylaminobenzylidenequinaldine*, $C_{19}H_{18}N_2$, crystallises from alcohol in pale yellow plates, or from benzene in brownish-yellow, flat needles melting at 177°. The *platinichloride* and *picrate* have been prepared.

p-*Aminobenzylidenequinaldine* melts at 154°, and its *hydrochloride* forms pale red needles, which become deep red when dry and melt at 273°. It dyes cotton mordanted with tannic acid a brilliant red. J. J. S.

Preparation and Hydrogenation of 1-Methyl-β-naphthindole. Robert Pschorr and Walther Karo (*Ber.*, 1906, **39**, 3140—3144).—β-Naphthylmethylamine is obtained conveniently by the methylation of acet-β-naphthalide or of the benzenesulphonamide, followed by hydrolysis of the product. The *hydrochloride* melts at 182—183° (corr.), the *picrate* at 145° (corr.), and the *phenylcarbamide* at 133—134° (corr.).

Sodium 1-*methyl-β-naphthindolesulphonate*, $C_{13}H_{10}N\cdot SO_3Na$, obtained by Hinsberg's method (Abstr., 1895, i, 144), melts at 169° (corr.), and by hydrolysis yields 1-*methyl-β-naphthindole*,

$$CH\begin{matrix}\diagup\!\!\!\diagup CH\text{—}\underset{\|}{C}\text{——————}\diagdown \\ \diagdown NMe\cdot C\cdot CH\!:\!CH\diagup\end{matrix}C_6H_4,$$

which melts at 53° and forms a red *picrate* melting at 172—173° (corr.). By reduction of an alcoholic solution of the naphthindole by zinc and hydrogen chloride, 1-*methyldihydro-β-naphthindole* is obtained quantitatively; it melts at 40—41°. The *hydrochloride* melts at 205—206° (corr.), the *picrate* at 158° (corr.), the *methiodide* at 220—221° (corr.). The dihydrogenated base is converted by sodium and amyl alcohol into the *ar*-tetrahydro *compound*, $C_{13}H_{17}N$, which boils at 160—180° under 14 mm. pressure, and does not form a carbonate. The *hydrochloride* melts at 186—187° (corr.), the *picrate* at 169° (corr.), the *methiodide* at 236—237° (corr.). The tertiary base is regenerated from the picrate by alcoholic potash at 160°.

C. S.

Synthesis in the Acridine Series. CARLO BAEZNER and AUGUST GARDIOL (*Ber.*, 1906, **39**, 2623—2625. Compare Abstr., 1904, i, 928; this vol., i, 699, 901).—The condensation product from aniline and *o*-nitrobenzyl chloride undergoes a change similar to that of *o*-nitrobenzyl chloride itself, which, when reduced by stannous chloride in the presence of primary or secondary amines and β-naphthol, yields acridine derivatives.

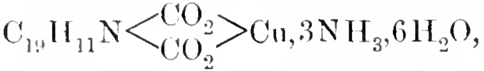
When *o*-nitrobenzyl chloride and aniline are warmed together, the main product is *o*-nitrobenzylaniline, whilst phenyl *o*-dinitrobenzylamine is also produced. When *o*-nitrobenzylaniline is reduced in alcoholic solution with aluminium amalgam, it forms *o*-aminobenzylaniline, $NHPh\cdot CH_2\cdot C_6H_4\cdot NH_2$, which crystallises from a mixture of water and alcohol in tiny needles and melts at 81°. When condensed with β-naphthol, it forms 1 : 2-phenonaphthacridine, melting at 132°, and identical with the product which Ullmann and Baezner (Abstr., 1902, i, 694) had previously obtained from *o*-aminobenzyl alcohol and β-naphthol.

In an analogous manner, 7-hydroxy-1 : 2-phenonaphthacridine, previously obtained by Baezner (Abstr., 1904, i, 928), may be prepared from *o*-aminobenzylaniline and 2 : 7-dihydroxynaphthalene. A characteristic reaction of this compound is the behaviour of its methiodide towards ammonia when the *compound* $C_{18}H_{13}ON$ is formed; the latter is dark blue, is insoluble in alkali, and melts at 227°. A. McK.

Syntheses in the Quinoline Group; Phenylnaphthaquinolinedicarboxylic Acid and its Derivatives. LOUIS J. SIMON and CH. MAUGUIN (*Compt. rend.*, 1906, **143**, 427—430).—The compound

$C_{25}H_{21}O_4N$, prepared by oxidising the cyclic compound obtained by the elimination of H_2O from the condensation product of ethyl oxalacetate and benzylidene β-naphthylamine (Abstr., 1904, i, 812), is *ethyl-2-phenyl-β-naphthaquinoline-3 : 4-dicarboxylate*,

$$C_{10}H_6{<}\begin{matrix}C(CO_2Et)\\N{=\!=}CPh\end{matrix}{>}C\cdot CO_2Et;$$

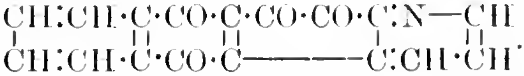
it melts at 128°, can be distilled under reduced pressure at 305°, and is not changed by warming with concentrated hydrochloric or sulphuric acid or potassium hydroxide solution. The *acid*, $C_{19}H_{11}N(CO_2H)_2$, obtained from the ester by prolonged heating (fifteen hours) with a 15 per cent. alcoholic solution of potassium hydroxide, forms pale yellow, microscopic needles insoluble in water or the ordinary solvents. It can be titrated in the presence of phenolphthalein, yielding the alkali salt from which the *silver*, *copper*, *lead*, *calcium*, and *barium* salts have been prepared by double decomposition. The *copper ammonium* salt,  $C_{19}H_{11}N{<}\begin{matrix}CO_2\\CO_2\end{matrix}{>}Cu,3NH_3,6H_2O$, forms deep blue, brilliant prisms. The *anhydride*,  $C_{19}H_{11}N{<}\begin{matrix}CO\\CO\end{matrix}{>}O$, obtained by fusing the acid at 218°, crystallises from boiling acetic acid or anhydride in golden yellow needles which melt at 218°, and yields the potassium salt of the acid by the action of aqueous or alcoholic potassium hydroxide, and the *ethyl hydrogen* ester, $CO_2H\cdot C_9H_{11}N\cdot CO_2Et,EtOH$, on boiling with absolute alcohol. The same ester is also obtained when the diethyl ester is heated for five hours with a 2 per cent. alcoholic solution of potassium hydroxide; it forms massive, rhombic, highly refractive crystals of an amber-yellow colour, loses its alcohol of crystallisation at 115°, and crystallises from methyl alcohol in long, white, silky needles containing 1 mol. of methyl alcohol of crystallisation. 2-Phenyl-β-naphthaquinoline (compare Döbner and Kuntze, Abstr., 1889, 411, 412) is obtained by heating 2-phenyl-β-naphthaquinoline-3 : 4-dicarboxylic acid or any of its derivatives with soda lime.

M. A. W.

Syntheses in the Quinoline Group; Ethyldihydrophenylnaphthaquinolinedicarboxylate and its Derivatives. Louis J. Simon and Charles Mauguin (*Compt. rend.*, 1906, **143**, 466—468. Compare preceding abstract).—The yellow compound, $C_{25}H_{23}O_4N$, melting at 146—147°, obtained by the elimination of H_2O from the condensation product of ethyl oxalacetate, benzaldehyde, and β-naphthylamine (Abstr., 1904, i, 812), is probably ethyl dihydrophenylnaphthaquinolinedicarboxylate; it is not attacked by hot concentrated aqueous potassium hydroxide, but is decomposed by fusing with potassium hydroxide, yielding a mixture of 2-phenylnaphthaquinoline, $C_{19}H_{13}N$, and 2-phenylnaphthaquinoline-4-carboxylic acid, $C_{19}H_{12}N\cdot CO_2H$, identical with the compounds prepared by Döbner (Abstr., 1889, 411, 412). 2-*Phenylnaphthaquinoline trichloroacetate*, $C_{19}H_{13}N_3,2(CCl_3\cdot CO_2H)$, is a characteristic salt, and the *copper ammonium* salt of 2-phenylnaphthaquinoline-4-carboxylic acid crystallises in small, blue prisms, and the *methyl* ester of the acid obtained by the action of methyl sulphate melts at 128° and is not changed by boiling with concentrated potassium hydroxide.

M. A. W.

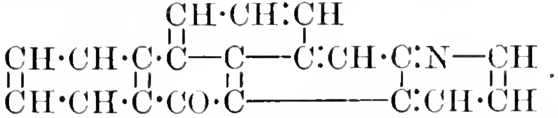
Preparation of an Oxidation Product of Alizarin-blue. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 171836).—Energetic oxidation of alizarin-blue leads to the disruption of the anthraquinone nucleus and the formation of phthalic acid. When alizarin-blue in solution, or suspension in water, is treated with mild oxidising agents either in neutral or acid solution it becomes converted into a yellow *compound* of quinonoid character, which in all probability has the following constitution:



$$\begin{array}{l} \mathrm{CH{:}CH{\cdot}C{\cdot}CO{\cdot}C{\cdot}CO{\cdot}CO{\cdot}C{:}N{-}CH} \\ \mathrm{CH{:}CH{\cdot}C{\cdot}CO{\cdot}C{-\!-\!-\!-}C{:}CH{\cdot}CH} \end{array}.$$

This substance, which is called *alizarin-blue quinone*, is reconverted into alizarin-blue by mild reducing agents, whilst treatment with ammonia transforms it into *alizarin-blue-amide*. Chlorine, bromine, hypochlorites, manganese dioxide, lead peroxide, and dilute nitric acid may be employed as oxidising agents, but when the last of these is used the product is a salt-like compound of the ortho-quinone and the acid which evolves nitrous fumes on warming with glacial acetic acid, whilst pure alizarin-blue quinone itself separates in well-defined crystals on cooling the solution or on adding alcohol. G. T. M.

Preparation of Benzanthronequinolines. Badische Anilin- & Soda-Fabrik (D.R.-P. 171939).—Although β-aminoalizarin when condensed with glycerol yields alizarin-blue, the quinoline of alizarin, yet this condensation when applied to β-aminoanthraquinone results in the formation of substances containing two new rings, $C_{14}H_9O_2N + 2C_3H_8O_3 = C_{20}H_{11}ON + 7H_2O$. The principal product, which is called *benzanthronequinoline*, probably has the following constitution:



$$\begin{array}{l} \qquad\quad\ \mathrm{CH{\cdot}CH{:}CH} \\ \mathrm{CH{\cdot}CH{\cdot}C{\cdot}C{-}C{-}C{:}CH{\cdot}C{:}N{-}CH} \\ \mathrm{CH{\cdot}CH{\cdot}C{\cdot}CO{\cdot}C{-\!-\!-\!-}C{:}CH{\cdot}CH} \end{array}.$$

When crystallised from toluene this substance separates in well-defined yellow needles melting at 251°. Another product of this condensation which melts at 232—234° is not homogeneous, because by fractional crystallisation it may be resolved into benzanthronequinoline, and another substance, $C_{17}H_9O_2N$, which melts at 322° and is isomeric with Graebe's anthraquinonequinoline.

Similar condensation products may be obtained from 2:6- and 2:7-diaminoanthraquinones and the sulphonic acids of the mono- and di-aminoanthraquinones. G. T. M.

Supposed Penthiazole Derivatives. Siegmund Gabriel and James Colman (*Ber.*, 1906, **39**, 2889—2892. Compare Gadamer, Abstr., 1896, i, 415; Gabriel and Hoisch, *ibid.*, 1897, i, 136).—Dixon's bromoethoxypenthiazoline (Trans., 1896, **69**, 31) is regarded as ethoxybromomethylthiazoline,  $\begin{array}{l}\mathrm{CH_2Br{\cdot}CH{-}S}\\ \qquad\ \ \mathrm{CH_2{\cdot}N}\end{array}\!\!\!>\!\mathrm{C{\cdot}OEt}$, since when oxidised with bromine water it yields *bromomethyltaurine*,

$$NH_2{\cdot}CH_2{\cdot}CH(CH_2Br){\cdot}SO_3H,$$

which crystallises from water in rectangular plates melting and decomposing at 273°. When reduced with zinc and sulphuric acid, the bromo-derivative yields β-methyltaurine. Bromomethyltaurine yields a *potassium* salt, $C_3H_7O_3NSBrK$, in the form of colourless, glistening plates, it dissolves readily in water, and when the solution is heated potassium bromide and *trimethyleneiminesulphonic acid*,  $NH{<}\substack{CH_2\\CH_2}{>}CH\cdot SO_3H$, are formed. The latter sinters at 230°, melts at about 245—247° and decomposes at 255—263°. When boiled with hydrobromic acid, it is reconverted into bromomethyltaurine or with hydriodic acid into iodomethyltaurine. J. J. S.

[3′-Chloro-4′-methylamino-4-hydroxydiphenylamine.] CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 172079).

—*p*-Aminophenol and 2-chloromethylaniline are oxidised with sodium dichromate in acid solution, when the indophenol, $NHMe\cdot C_6H_3Cl\cdot N\colon C_6H_4\colon O$, thus produced, separates rapidly and partly in a crystalline condition. This colouring matter dissolves in alcohol to an intense blue solution; when treated with warm sodium sulphide in alkaline solution it is reduced, yielding *3′-chloro-4′-methylamino-4-hydroxydiphenylamine*,

$$NHMe\cdot C_6H_3Cl\cdot NH\cdot C_6H_4\cdot OH,$$

a base which melts at 105° and yields a hydrochloride crystallising in greyish-white needles. *3′-Chloro-4′-methylamino-4-ethoxydiphenylamine*, $NHMe\cdot C_6H_3Cl\cdot NH\cdot C_6H_4\cdot OEt$, melts at 115°. Further action of sodium sulphide on these bases at higher temperatures leads to the production of blue sulphur colouring matters. G. T. M.

Transformations of Hydrocyanocarbodiphenylimide. GUSTAV SCHULTZ, GEORG ROHDE, and GUSTAV HERZOG (*J. pr. Chem.*, 1906, [ii], 74, 74—91).

—When dissolved in concentrated sulphuric acid, hydrocyanocarbodiphenylimide gradually forms an orange-yellow solution and is regained almost quantitatively on dilution. If the solution in concentrated sulphuric acid is heated on the water-bath, the hydrocyano-compound is partially hydrolysed, yielding phenyloxamide and diphenylamidineoxamide. If the heating is prolonged, the hydrocyanocarbodiphenylimide is hydrolysed to aniline, oxalic acid, and ammonia, the aniline being partially sulphonated; only traces of isatin α-anilide are formed.

Diphenylamidineoxamide, $NHPh\cdot C(NPh)\cdot CO\cdot NH_2$, crystallises in large, glistening, yellow leaflets, melts at 155°, and, when heated above its melting point, resolidifies, forming yellow leaflets melting and decomposing at about 302°; the solution in dilute sulphuric acid deposits phenyloxamide slowly at the ordinary temperature, but quickly if heated; when heated with aqueous sodium hydroxide, the amidineoxamide is hydrolysed, forming aniline, oxalic acid, and ammonia. On treatment with aqueous sodium nitrite in cold concentrated sulphuric acid solution, diphenylamidineoxamide yields phenyloxamide and *p-nitrophenyloxamide*, $NO_2\cdot C_6H_4\cdot NH\cdot C_2O_2\cdot NH_2$, which is formed also by the action of aqueous ammonia on ethyl *p*-nitrophenyloxamate. It crystallises from pyridine in slender, yellowish-grey needles, melts and decomposes at 308—310°, is stable towards acids, and is hydrolysed by aqueous alkali hydroxides, forming *p*-nitroaniline, oxalic acid, and ammonia. *Ethyl* p-*nitrophenyloxamate*, $NO_2\cdot C_6H_4\cdot NH\cdot CO\cdot CO_2Et$, is prepared together with a *product* (*di*-p-*nitro-oxanilide?*) melting above 360°, by heating a molecular mixture of *p*-nitroaniline and ethyl oxalate in a reflux apparatus; it crystallises in almost colourless, voluminous, long needles, melts at 171°, and is hydrolysed by aqueous sodium hydroxide, forming *p*-nitroaniline, oxalic acid, and ethyl alcohol. The action of nitrogen trioxide or of nitric acid on diphenylamidineoxamide in concentrated sulphuric acid solution leads to the formation of *p*-nitrophenyloxamide and *di*-p-*nitrophenylamidineoxamide*,

$$NO_2\cdot C_6H_4\cdot NH\cdot C(CO\cdot NH_2)\colon N\cdot C_6H_4\cdot NO_2\ ;$$

this crystallises in greenish-yellow, transparent prisms, melts and decomposes at 245°, is readily soluble in pyridine, when boiled with glacial acetic acid in a reflux apparatus yields *p*-nitrophenyloxamide, and is hydrolysed by aqueous sodium hydroxide, forming *p*-nitroaniline, oxalic acid, and ammonia.

Hydrocyanocarbodi-p-*nitrophenylimide*,

$$NO_2\cdot C_6H_4\cdot NH\cdot C(CN)\colon N\cdot C_6H_4\cdot NO_2,$$

prepared by the action of nitric acid on hydrocyanocarbodiphenylimide in cooled concentrated sulphuric acid solution, is obtained in two modifications, of which the labile crystallises from dilute solutions in transparent, greenish-yellow, rhombic leaflets or plates, and when heated at 110° changes into the stable form; this is formed on rapid separation from a concentrated solution and crystallises in matted, thin, yellow needles. Both modifications melt and decompose at 217°, and yield *p*-nitrophenyloxamide and *p*-nitroaniline when heated with concentrated sulphuric acid at 120—140°; hydrolysis by means of boiling dilute sulphuric acid leads to the formation of *p*-nitroaniline, ammonia, and oxalic acid. The *sodium* derivative,

$$NO_2\cdot C_6H_4\cdot NNa\cdot C(CN)\colon N\cdot C_6H_4\cdot NO_2,$$

is intensely red and yields the free nitrile when treated with dilute sulphuric acid or persistently washed with water. When heated with aqueous sodium hydroxide, hydrocyanocarbodi-*p*-nitrophenylimide yields small quantities of ammonia and *p*-nitroaniline together with a *mixture* of two substances, one of which was identified as di-*p*-nitrophenylcarbamide.

When heated with dilute sulphuric acid, hydrocyanocarbodiphenylimide yields aniline and oxanilonitrile (cyanoformanilide), which melts and decomposes at 128° (120°: Dieckmann and Kaemmerer, Abstr., 1905, i, 874) and is hydrolysed by hot concentrated sulphuric acid, forming phenyloxamide.

The action of sodium nitrite on hydrocyanocarbodiphenylimide in glacial acetic acid solution leads to the formation of *nitrosocyanocarbodiphenylimide*, $NO\cdot NPh\cdot C(CN)\colon NPh$, which separates in stout, yellow crystals, melts and decomposes at 117—118°, and gives the reactions of hydrocyanocarbodiphenylimide, into which it decomposes on recrystallisation. G. Y.

Additive Products of Derivatives of Trinitrobenzene with Certain Aromatic Nitrogen Compounds. RICCARDO CIUSA and C. AGOSTINELLI (*Atti R. Accad. Lincei*, 1906, [v], **15**, ii, 238—242).—The phenylhydrazones of acetone, propaldehyde, and camphor, and probably those of all aliphatic aldehydes and ketones, readily yield crystalline picrates, the formation of which may be used for characterising small quantities of aldehydes and ketones of the aliphatic series.

Picryl chloride reacts with propaldehydephenylhydrazone, and probably with the phenylhydrazones of all aliphatic aldehydes and ketones, yielding *s*-picrylphenylhydrazine, $RCH\!:\!N\cdot NHPh + H_2O + C_6H_2Cl(NO_2)_3 = R\cdot CHO + HCl + C_6H_2(NO_2)_3\cdot NH\cdot NHPh$. With benzalazine, piperonalazine, benzylideneaniline, and cinnamylideneaniline, a similar reaction takes place, whilst with aldazines the corresponding trinitrophenylhydrazones are obtained according to the equation

$$CHR\!:\!N\cdot N\!:\!CHR + H_2O + C_6H_2Cl(NO_2)_3 = HCl + R\cdot CHO + C_6H_2(NO_2)_3\cdot NH\cdot N\!:\!CHR.$$

With Schiff's bases, picryl chloride reacts giving the corresponding picrylanilines: $CHR\!:\!NPh + H_2O + C_6H_2Cl(NO_2)_3 = HCl + R\cdot CHO + C_6H_2(NO_2)_3\cdot NHPh$.

Acetone phenylhydrazone picrate, $CMe_2\!:\!N_2HPh,C_6H_2(NO_2)_3\cdot OH$, crystallises from benzene in unstable, yellow needles melting at 81—82°.

Camphor phenylhydrazone picrate, $C_{10}H_{16}\!:\!N_2HPh,C_6H_2(NO_2)_3\cdot OH$, crystallises in golden-yellow needles melting at 137° to a black liquid.

Propaldehydephenylhydrazone picrate,

$$CH_2Me\cdot CH\!:\!N_2HPh,C_6H_2(NO_2)_3\cdot OH,$$

crystallises from alcohol in minute, canary-yellow needles melting at 156—157°.

The interaction of molecular proportions of propaldehydephenylhydrazone and picryl chloride in alcoholic solution yields trinitrohydrazobenzene, which melts at 186—187° (183—185°: Fischer, *Annalen*, 1889, **252**, 2); on boiling with 90 per cent. acetic acid the latter is converted into an isomeric *compound*, which crystallises in golden-yellow scales melting at 186°, and probably has the structure $NH_2\cdot C_6H_4\cdot NH\cdot C_6H_2(NO_2)_3$.

Picryl chloride and benzalazine yield benzaldehydetrinitrophenylhydrazone, which melts at 273—274°; Purgotti (Abstr., 1895, i, 27) gave the melting point 248°, and Curtius (Abstr., 1895, i, 30) 267°.

Piperonaldehydetrinitrophenylhydrazone,

$$C_6H_2(NO_2)_3\cdot N_2H\!:\!CH\cdot C_6H_3\!:\!O_2\!:\!CH_2,$$

prepared by the interaction of piperonalazine and picryl chloride, separates from acetic acid in dark red crystals melting at 169°.

The action of picryl chloride on cinnamylideneaniline yields cinnamaldehyde and picrylaniline. T. H. P.

Hydrazine Derivatives of the Diaminodiphenylmethane Series. HERMANN FINGER [with M. BAUMANN] (*J. pr. Chem.*, 1906, [ii], 74, 155—156).—The hydrazine derivatives of *pp'*-diaminodiphenylmethane and diaminoditolylmethane may be prepared by way of the diazosulphonates or the diazonium chlorides.

The *potassium diazosulphonate*, $C_{13}H_{10}O_6N_4S_2K_2$, obtained from *pp'*-diaminodiphenylmethane, separates in slender, yellow needles, and when reduced with zinc dust and boiling acetic acid, yields pp'-*dihydrazinodiphenylmethane*; this forms a white precipitate, crystallises from alcohol, and melts at 139—140°. The *hydrochloride*, $C_{13}H_{16}N_4,2HCl$, forms greyish-white leaflets; the *dinitroso*-derivative is slightly yellow and melts at 88°; the *disemicarbazide* crystallises in silvery leaflets and melts at 250°; the *condensation* product with acetone, $CH_2(C_6H_4·NH·N:CMe_2)_2$, melts at 90—91°, and when reduced with zinc chloride forms a *di-indylmethane*,  $CH_2\left(C_6H_3<\genfrac{}{}{0pt}{}{CH}{NH}>CMe\right)_2$, melting at 170—175°.

pp'-Dihydrazinodiphenylmethane hydrochloride condenses with ethyl acetoacetate, forming a *product* which at 150° is converted into the corresponding *pyrazolone* melting at 210°. G. Y.

Preparation of *s*-Secondary Hydrazines from Antipyrines.

Ludwig Knorr (*Ber.*, 1906, **39**, 3265—3267).—*s*-Phenylmethylhydrazine, formed in 85 per cent. yield from antipyrine and alcoholic potash at 130°, boils at 200—201° under 331 mm. and at 230° at the ordinary pressure; the *oxalate*, $C_7H_{10}N_2,C_2H_2O_4$, forms slender needles and melts and decomposes at 155—156°.

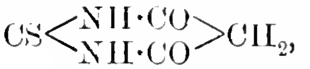
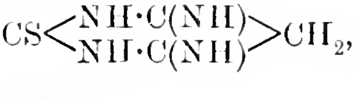
s-Phenylethylhydrazine, obtained from 1-phenyl-3-methyl-2-ethylpyrazolone in a similar manner, boils at 237—240° under 750 mm. pressure, and forms an *oxalate* which melts and decomposes at 167—168°.

1 : 2 : 3-Trimethylpyrazolone boils at 306—309° under 751 mm. pressure, forms a *platinichloride* which decomposes at 197—198°, and a *picrate* which melts and decomposes at 211—212°. Alcoholic potash at 190° converts the base into *s*-dimethylhydrazine, which boils at 80—81° under 753 mm. pressure (compare this vol., i, 817). C. S.

Crystallographic Constants of 4-Chloropyrazole.

Carlo Maria Viola (*Zeit. Kryst. Min.*, 1906, **42**, 384—385).—Determinations are given for this substance, obtained by G. Mazzara and A. Borgo by the action of sulphuryl chloride on pyrazole. L. J. S.

Preparation of 4 : 6-Dioxy-2-thiopyrimidine and its 5-Alkyl Substituents.

Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 171292).—4 : 6-Dioxy-2-thiopyrimidine,  $CS<\genfrac{}{}{0pt}{}{NH·CO}{NH·CO}>CH_2$, was prepared by heating 4 : 6-di-imino-2-thiopyrimidine,  $CS<\genfrac{}{}{0pt}{}{NH·C(NH)}{NH·C(NH)}>CH_2$, with 30 per cent. sulphuric acid.

4 : 6-Dioxy-2-thio-5-diethylpyrimidine,  $CS<\genfrac{}{}{0pt}{}{NH·CO}{NH·CO}>CEt_2$, was obtained in a similar manner from 4 : 6-diamino-2-thio-5 : 5-diethylpyrimidine (compare Abstr., 1905, i, 671). G. T. M.

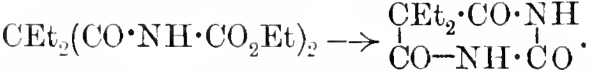
Preparation of Barbituric Acid and its 5-Alkyl Derivatives.

Chemische Fabrik auf Aktien (vorm. E. Schering) (D.R.-P. 171294).—Ethyl malonamate and urethane were condensed by heating on the water-bath with alcoholic sodium ethoxide, and the resulting barbituric acid precipitated from the acidified solution. The corresponding *C*-alkyl derivatives were similarly prepared from the mono- and di-alkylmalonamates. G. T. M.

Preparation of 5:5-Dialkylbarbituric Acid. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 170907).—The 5:5-dialkylbarbituric acids are obtained from the corresponding thio-derivatives by heating these with solutions of the salts of the heavy metals.

Diethylthiobarbituric acid, when boiled for twenty-four to forty-eight hours with solutions of lead acetate or copper chloride, yielded a precipitate of the metallic sulphide, and the diethylbarbituric acid was then isolated on concentrating the filtered solution. G. T. M.

Preparation of 5:5-Dialkylbarbituric Acids. WILHELM TRAUBE (D.R.-P. 171992).—The diurethane derivatives of the dialkylmalonic acids are produced by heating the dialkylmalonyl chlorides with urethanes: $\mathrm{CEt_2(COCl)_2 + 2NH_2{\cdot}CO_2Et = CEt_2(CO{\cdot}NH{\cdot}CO_2Et)_2 + 2HCl}$. These products, when heated at temperatures varying from 80° to 150° with metallic alkyloxides, either alone or in alcoholic solution, are readily converted into dialkylbarbituric acids:



$$\mathrm{CEt_2(CO{\cdot}NH{\cdot}CO_2Et)_2} \longrightarrow \begin{array}{l}\mathrm{CEt_2{\cdot}CO{\cdot}NH}\\ \;| \qquad\qquad\; | \\ \mathrm{CO{-}NH{\cdot}CO}\end{array}.$$

For example, 30 parts of diethylmalonylurethane, when heated with 7 to 20 parts of dry sodium ethoxide for one or two hours at 80—100° and then at 150°, and subsequently treated with dilute acid, yield diethylbarbituric acid melting at 191°. G. T. M.

Preparation of 5:5-Dialkylbarbituric Acids. WILHELM TRAUBE (D.R.-P. 172885, 172886. Compare this vol., i, 538, and preceding abstracts).—Instead of heating the dialkylmalonyldiurethanes with metallic alkyloxides, the conversion of these substances into 5:5-dialkylbarbituric acids may be readily effected by heating with alcoholic or aqueous alkali hydroxides or with concentrated or fuming sulphuric acid. This transformation may likewise be carried out by the agency of aqueous or alcoholic ammonia or organic bases.

Diethylmalonyldiurethane mixed with ordinary concentrated sulphuric acid is added to fuming sulphuric acid and heated at 100° for some time. On pouring the solution into ice-cold water, 5:5-diethylbarbituric acid separates as an oil which rapidly solidifies. This acid is also formed when the diurethane is boiled with alcoholic potash, soda, ammonia, or any organic base such as guanidine, pyridine, or an alkylamine. G. T. M.

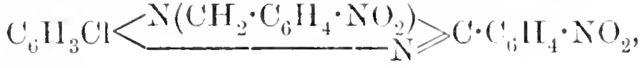
Preparation of Guanyldiethylbarbituric Acid. CHEMISCHE FABRIK VON HEYDEN AKTIEN-GESELLSCHAFT (D.R.-P. 171147).—*Guanyldiethylbarbituric acid,*  $\mathrm{CO}\Big\langle\begin{array}{l}\mathrm{NH{-}CO}\\ \mathrm{CEt_2{\cdot}CO}\end{array}\Big\rangle\mathrm{N{\cdot}C(NH_2){:}NH}$ or

$$\mathrm{CO}\Big\langle\begin{array}{l}\mathrm{NH{-}CO{\cdot}NH}\\ \mathrm{CEt_2{\cdot}CO{\cdot}NH}\end{array}\Big\rangle\mathrm{C{:}NH},$$

is prepared by heating together ethyl diethylmalonate and dicyanodiamidine hydrochloride in alcoholic sodium ethoxide and slightly acidifying the solution; when crystallised from hot, dilute hydrochloric acid, it separates in well-defined prisms. Prolonged boiling with mineral acids hydrolyses the guanyl derivatives to diethylbarbituric acid. The condensation may also be effected by means of sodamide or metallic sodium. G. T. M.

Benziminazoles and their Resolution. OTTO FISCHER and FRITZ LIMMER (*J. pr. Chem.*, 1906, [ii], 74, 57—73. Compare Fischer and Hess, Abstr., 1904, i, 195; Fischer, this vol., i, 539).—p-*Chlorodibenzylidene*-o-*phenylenediamine*, $C_6H_3Cl(N:CHPh)_2$, formed from *p*-chloro-*o*-phenylenediamine and benzaldehyde at 150—170°, crystallises in colourless, nodular aggregates, melts at about 168°, and on prolonged heating above its melting point yields 6-*chloro* 2-*phenyl*-1-*benzylbenziminazole*, $C_6H_3Cl<\frac{N(CH_2Ph)}{N}>CPh$, which crystallises from alcohol in white needles and volatilises at about 225°. The *hydrochloride* forms slender, white needles; the *platinichloride* crystallises in short, yellow needles; the *nitrate* crystallises in long, colourless prisms.

p-*Chlorodi*-p-*nitrobenzylidene*-o-*phenylenediamine*, prepared from *p*-chloro-*o*-phenylenediamine and *p*-nitrobenzaldehyde, crystallises in red leaflets, melts at about 150°, and gradually becomes yellow, forming 6-*chloro*-2-p-*nitrophenyl*-1-p-*nitrobenzylbenziminazole*,



$$C_6H_3Cl<\frac{N(CH_2\cdot C_6H_4\cdot NO_2)}{N}>C\cdot C_6H_4\cdot NO_2,$$

which melts at 235°.

The *product* obtained on shaking *p*-chloro-*o*-phenylenediamine with ethyl acetoacetate in alcoholic solution crystallises in long, white needles, melts at 140°, forms a *nitrobenzylidene* derivative crystallising in reddish-yellow needles and melting at 210°, and on prolonged heating above its melting point is converted into ethyl acetate and 6-*chloro*-2-*methylbenziminazole*, $C_6H_3Cl<\frac{NH}{N}>CMe$, which melts at 203°.

p-*Chlorodiphenylquinoxaline*, $C_{20}H_{13}N_2Cl$, prepared by heating a molecular mixture of *p*-chloro-*o*-phenylenediamine and benzil at 100°, crystallises in colourless, refracting leaflets, melts at 130°, and gives a red coloration with concentrated sulphuric acid.

p-*Chloro*-o-*phenylenethiocarbamide*, $C_6H_3Cl<\frac{NH}{NH}>CS$, prepared by boiling *p*-chloro-*o*-phenylenediamine with a concentrated aqueous solution of ammonium thiocyanate and a small quantity of hydrochloric acid and heating the product at 130—150°, crystallises in colourless needles, melts above 270°, is almost insoluble in water, but dissolves readily in alcohol, and has a bitter taste.

p-*Chloro*-o-*phenylenecarbamide*, $C_6H_3Cl<\frac{NH}{NH}>CO$, obtained by heating *p*-chloro-*o*-phenylenediamine with phosgene in toluene solution, crystallises in small, white needles, melts above 270°, and has a bitter taste.

p-*Chloronitrodiacetyl*-o-*phenylenediamine*, $C_{10}H_{10}O_4N_3Cl$, is prepared by adding *p*-chlorodiacetyl-*o*-phenylenediamine, which melts at 208° (201°: Ullmann and Mauthner, Abstr., 1904, i, 192) to red, fuming nitric acid; it crystallises in stellate aggregates of needles, softens at about 240°, melts and decomposes at 245°, has weak basic and acid properties, and gives a deep red coloration with concentrated alkali hydroxides.

p-*Chlorodibenzoyl*-o-*phenylenediamine*, $C_{20}H_{15}O_2N_2Cl$, formed by fusing the *o*-diamine with benzoic anhydride, crystallises in soft, silky needles, melts at 230°, and is insoluble in dilute acids or alkali hydroxides. p-*Chloronitrodibenzoyl*-o-*phenylenediamine*, prepared by the action of fuming nitric acid on the preceding substance, crystallises in nodular aggregates of almost colourless needles, melts at 209—210°, dissolves in concentrated hydrochloric or sulphuric acid, and with concentrated potassium hydroxide gives a red coloration, becoming yellow on exposure to air.

6-*Chloronitrobenziminazole*, $NO_2\cdot C_6H_2Cl<\substack{NH \\ N}>CH$, prepared by dissolving 6-chlorobenziminazole (Fischer, Abstr., 1904, i, 349) in red, fuming nitric and concentrated sulphuric acids, crystallises in small, slightly yellow needles, melts at 180—181°, and is readily soluble in cold aqueous alkali hydroxides or ammonia, mineral acids, glacial acetic acid, or hot alcohol. When heated with methyl iodide and methyl alcohol in a sealed tube at 110°, it yields the quaternary *iodide*, $NO_2\cdot C_6H_2Cl<\substack{N(MeI) \\ NMe}>CH$, which crystallises in yellow prisms, and the *periodide*, $C_9H_9O_2N_3ClI_3$, which is obtained in blue, glistening prisms, and loses I_2 when boiled with water, or more quickly when treated with sulphur dioxide or aqueous alkali hydroxides. 6-*Chloronitro*-1 : 3-*dimethylbenziminazolol*, $NO_2\cdot C_6H_2Cl<\substack{NMe \\ NMe}>CH\cdot OH$, prepared by heating the quaternary iodide with an aqueous alkali hydroxide, crystallises from alcohol in yellow leaflets, becomes brown at about 190°, melts and decomposes at about 215°, and is moderately soluble in hot water. p-*Chloronitrodimethyl*-o-*phenylenediamine*, $C_8H_{10}O_2N_3Cl$, obtained on boiling the carbinol with alcoholic potassium hydroxide for half an hour, crystallises in red prisms, melts at 220°, forms a yellow *ferrichloride* and a *hydrochloride* crystallising in slender, yellow needles, regenerates the benziminazolol when boiled with concentrated formic acid, and yields 6-chloronitro-1 : 2 : 3-trimethylbenziminazole when boiled with glacial acetic acid and acetic anhydride.

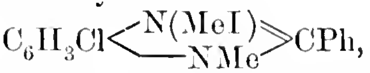
6-*Chloronitro-2-methylbenziminazole*, $NO_2\cdot C_6H_2Cl<\substack{NH \\ N}>CMe$, prepared by heating *p*-chloronitrodiacetyl-*o*-phenylenediamine with concentrated hydrochloric acid on the water-bath, or by nitrating 6-chloro-2-methylbenziminazole, crystallises from dilute alcohol in almost colourless needles, melts at 210°, and is readily soluble in aqueous alkali hydroxides, ammonia, glacial acetic acid, or alcohol. The *aurichloride* forms large, golden prisms, the *platinichloride*, long, light-yellow needles, and the *picrate*, long, yellow prisms melting at 221°.

6-*Chloronitro*-1 : 2 : 3-*trimethylbenziminazolium iodide*,

$$C_{10}H_{11}O_2N_3ClI,$$

formed together with the brown, crystalline *periodide* when 6-chloronitro-2-methylbenziminazole is heated with methyl iodide and methyl alcohol at 110° under pressure, crystallises in long, yellow needles and melts at 263°. 6-*Chloronitro*-1 : 2 : 3-*trimethylbenziminazolol*,  $NO_2\cdot C_6H_2Cl<\genfrac{}{}{0pt}{}{NMe}{NMe}>CMe\cdot OH$, prepared by gently heating the quaternary iodide with aqueous potassium hydroxide, crystallises from hot alcohol in glistening, yellow leaflets, becomes brown at about 190°, melts at about 205°, and when boiled with alcoholic potassium hydroxide is hydrolysed, yielding acetic acid and *p*-chloronitrodimethyl-*o*-phenylenediamine.

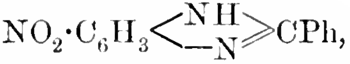
6-*Chloro-2-phenylbenziminazole*,  $C_6H_3Cl<\genfrac{}{}{0pt}{}{NH}{N}>CPh$, prepared by heating *p*-chlorodibenzoyl-*o*-phenylenediamine with concentrated hydrochloric acid at 160° under pressure, crystallises in glistening, colourless leaflets, melts at 210°, and is readily soluble in alcohol, hot ether, chloroform, or hot aqueous alkali hydroxides.

The quaternary *iodide*,  $C_6H_3Cl<\genfrac{}{}{0pt}{}{N(MeI)}{NMe}>CPh$, forms glistening leaflets, melts at 263°, and when boiled with aqueous or alcoholic potassium hydroxide is converted into the *carbinol*,

$$C_6H_3Cl<\genfrac{}{}{0pt}{}{NMe}{NMe}>CPh\cdot OH,$$

which crystallises from dilute alcohol in colourless, quadratic prisms, melts at 140°, and is only slightly hydrolysed by boiling alcoholic potassium hydroxide.

6-*Chloronitro-2-phenylbenziminazole*, $C_{13}H_8O_2N_3Cl$, prepared from *p*-chloronitrodibenzoyl-*o*-phenyldiamine or by nitration of 6-chloro-2-phenylbenziminazole, crystallises in yellow needles, melts at 255°, and is readily soluble in hot alcohol, glacial acetic acid, or aqueous alkali hydroxides or ammonia. 6-*Chloro-2-phenyl*-1 : 3-*dimethylbenziminazolium iodide* crystallises in colourless needles and melts at 265—266°. The *carbinol*, $C_{15}H_{14}O_3N_3Cl$, crystallises in glistening, golden leaflets, melts at 188°, and on prolonged boiling with alcoholic potassium hydroxide yields benzoic acid and *p*-chloronitrodimethyl-*o*-phenylenediamine.

Huebner's nitrophenylbenziminazole (Abstr., 1881, 1131) is 6-nitro-2-phenylbenziminazole,  $NO_2\cdot C_6H_3<\genfrac{}{}{0pt}{}{NH}{N}>CPh$, as on methylation it yields a quaternary *iodide*, $C_{15}H_{14}O_2N_3I$, which crystallises in stellate groups of needles, melts at 249°, and when boiled with alcoholic potassium hydroxide is converted into 6-*nitro-2-phenyl*-1 : 3-*dimethylbenziminazolol*,  $NO_2\cdot C_6H_3<\genfrac{}{}{0pt}{}{NMe}{NMe}>CPh\cdot OH$; this crystallises in golden leaflets, melts at 192°, and on hydrolysis yields benzoic acid and *m*-nitrodimethyl-*o*-phenylenediamine.

2-o-*Nitrophenyl*-1 : 3-*dimethylbenziminazolium iodide*, $C_{15}H_{14}O_2N_3I$, prepared from 2-*o*-nitrophenylbenziminazole, crystallising in colourless prisms (brown leaflets: Walther and Pulawski, Abstr., 1899, i, 639), crystallises in red, dichroic octahedra, forms a yellow powder when pulverised, melts above 280°, and when warmed with aqueous potassium hydroxide forms the *carbinol*. This crystallises in large, orange prisms, melts at 210°, and yields only traces of *s*-dimethyl-*o*-phenylenediamine on prolonged boiling with alcoholic potassium hydroxide.

2-m-*Nitrophenyl*-1 : 3-*dimethylbenziminazolium iodide* crystallises in flat, yellow needles and melts at high temperatures. 2-m-*Nitrophenyl*-1 : 3-*dimethylbenziminazolol*, $C_{15}H_{15}O_3N_3$, crystallises in yellow needles, melts at 167°, and is hydrolysed to only a slight extent when boiled with alcoholic potassium hydroxide for several hours.

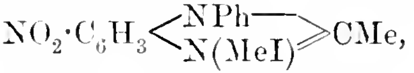
2-*p*-Nitrophenylbenziminazole melts at 210° (compare Walther and Pulawski, *loc. cit.*); the quaternary *iodide* formed by heating with methyl iodide crystallises in long, yellow needles, melts above 270°, and when treated with an alkali hydroxide yields 2-p-*nitrophenyl*-1 : 3-*dimethylbenziminazolol*, which crystallises in yellow prisms and melts at 140°.

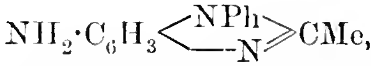
The yellow quaternary iodides described above form colourless aqueous solutions. G. Y.

Some Benziminazoles from 4 : 2-Nitroaminodiphenylamine.

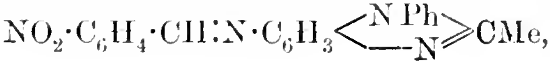
REINHOLD VON WALTHER and ALEX. KESSLER (*J. pr. Chem.*, 1906, [ii], 74, 188—206, 241—248. Compare Abstr., 1904, i, 318).—The *hydrochloride* of 5-nitro-1-phenyl-2-methylbenziminazole crystallises in glistening leaflets and melts at 228°; the *picrate*,

$$C_{14}H_{11}O_2N_3,C_6H_3O_7N_3,$$

forms yellow needles and does not melt at 270°; the *methiodide*,  $NO_2\cdot C_6H_3<\begin{matrix}NPh\\N(MeI)\end{matrix}>CMe$, crystallises in yellow prisms and commences to decompose at 270°. 5-*Nitro*-1-*phenyl*-2 : 3-*dimethylbenziminazolol*,  $NO_2\cdot C_6H_3<\begin{matrix}NPh\\NMe\end{matrix}>CMe\cdot OH$, prepared by heating the methiodide with aqueous sodium hydroxide, crystallises from benzene in yellow needles, melts at 206°, and is not hydrolysed by boiling alcoholic potassium hydroxide.

5-*Amino*-1-*phenyl*-2-*methylbenziminazole*,  $NH_2\cdot C_6H_3<\begin{matrix}NPh\\N\end{matrix}>CMe$, prepared by reduction of the 5-nitro-compound by means of alcoholic ammonium sulphide at 120° under pressure, crystallises from a mixture of ethyl acetate and light petroleum in yellowish-brown needles, melts at 145—147°, and is a strong base dissolving readily in dilute acids. The *picrate*, $C_{14}H_{13}N_3,C_6H_3O_7N_3$, melts at 195°; the *platinichloride* forms yellow needles and is unstable. The *acetyl* derivative, $NHAc\cdot C_7N_2H_3PhMe$, crystallises in white needles and melts at 229—230°. The *benzeneazo*-derivative, $NPh:N\cdot NH\cdot C_7N_2H_3PhMe$, formed by adding a freshly-prepared solution of diazobenzene chloride and sodium acetate to the amine in cooled hydrochloric acid solution, crystallises in yellowish-red needles, melts at 184—185°, is insoluble in aqueous sodium hydroxide, evolves nitrogen when heated with hydrochloric acid, and decomposes on prolonged heating with alcohol.

The p-*nitrobenzylidene* derivative,



$$NO_2\cdot C_6H_4\cdot CH:N\cdot C_6H_3<\begin{matrix}NPh\\N\end{matrix}>CMe,$$

formed by boiling the amine with *p*-nitrobenzaldehyde in alcoholic solution in a reflux apparatus, crystallises in yellow needles and melts at 240°. The o-*nitrobenzylidene* derivative, $C_{21}H_{16}O_2N_4$, crystallises from alcohol in green needles and melts at 153—155°.

When heated with resorcinol at 175°, 5-amino-1-phenyl-2-methylbenziminazole forms an *additive* compound, $C_{14}H_{13}N_3,C_6H_4(OH)_2$, which crystallises from dilute alcohol in silver-grey needles and melts at 197°. The *thiocarbamide*, $CS(NH\cdot C_7N_2H_3PhMe)_2$, prepared by heating the amine with carbon disulphide and a small quantity of flowers of sulphur in alcoholic solution in a sealed tube at 100°, crystallises from dilute alcohol in white needles, sinters at 130°, and melts and decomposes at 141°. 5-*Phenylcarbamido*-1-*phenyl*-2-*methylbenziminazole*, $NHPh\cdot CO\cdot NH\cdot C_7N_2H_3PhMe$, formed by the action of phenylcarbimide on the amine in ethereal solution, crystallises from alcohol and melts and decomposes at 140—143°.

4-*Nitro*-2-*formylaminodiphenylamine*, $CHO\cdot NH\cdot C_6H_3(NO_2)\cdot NHPh$, prepared by the action of anhydrous formic acid on 4-nitro-2-aminodiphenylamine at the ordinary temperature, crystallises from alcohol in golden needles, melts at 182°, and gives a characteristic deep violet coloration with concentrated sulphuric acid. When heated with 40 per cent. sulphuric acid on the water-bath, 4-nitro-2-formylaminodiphenylamine yields hydrated 5-nitro-1-phenylbenziminazole,

$$NO_2\cdot C_6H_3<\substack{NPh\\ N}>CH,2H_2O$$

(compare Reissert and Goll, Abstr., 1905, i, 247), which crystallises in colourless needles and melts at 134°; the anhydrous benziminazole obtained by heating the hydrated substance on the water-bath, or recrystallising it from alcohol, or by heating 4-nitro-2-aminodiphenylamine with an excess of ethyl-*o*-formate in a reflux apparatus on the water-bath, or by heating 4-nitro-2-formylaminodiphenylamine with hydrochloric acid, crystallises in colourless needles and melts at 156°. The *nitrate*, $C_{13}H_9O_2N_3,HNO_3$, crystallises in white needles, melts at 205°, and is sparingly soluble; the *platinichloride*,

$$(C_{13}H_9O_2N_3)_2,H_2PtCl_6,$$

forms yellow needles; the *methiodide*, $NO_2\cdot C_6H_3<\substack{NPh\\ N(MeI)}>CH$, crystallises in stout, yellow needles and commences to melt and decompose at 245°.

5-*Nitro*-1-*phenyl*-3-*methylbenziminazolol*,

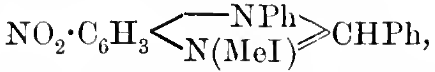
$$NO_2\cdot C_6H_3<\substack{NPh\\ NMe}>CH\cdot OH,$$

obtained by treating the methiodide with sodium hydroxide in cooled aqueous solution, crystallises in yellow needles and melts at 200°. When heated with alcoholic potassium hydroxide, the methiodide is hydrolysed, forming 4-nitro-2-methylaminodiphenylamine,

$$NO_2\cdot C_6H_3(NHMe)\cdot NHPh,$$

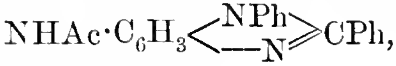
which crystallises from alcohol, is yellow, and melts at 155—156°. It is converted by boiling with acetic anhydride in glacial acetic solution into 5-nitro-1-phenyl-2 : 3-dimethylbenziminazolol, melting at 206°.

When heated with concentrated hydrochloric acid at 150°, 4-nitro-2-benzoylaminodiphenylamine, prepared by boiling 4-nitro-2-aminodiphenylamine with benzoic anhydride in alcoholic solution (compare Muttelet, Abstr., 1898, i, 412), is converted into the insoluble *hydrochloride* of 5-nitro-1 : 2-diphenylbenziminazole, $C_{19}H_{13}O_2N_3,HCl$, which crystallises in silvery needles melting at 236° ; the base melting at 181—182° is formed when 4-nitro-2-benzoylaminodiphenylamine is heated with dilute sulphuric acid at 100° and treated with concentrated sulphuric acid, or when 4-nitro-2-aminodiphenylamine is heated with benzoic anhydride at 180°. The *methiodide*,

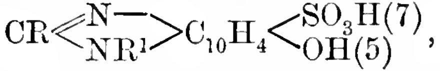


$$NO_2{\cdot}C_6H_3{<}\begin{matrix}\text{——NPh}\\ \text{N(MeI)}\end{matrix}{>}CHPh,$$

crystallises from methyl alcohol in yellow needles, commences to melt and decompose at 260°, and when treated with potassium hydroxide in hot methyl-alcoholic solution yields the yellow carbinol (?) melting at 190°, and, on further heating, 4-nitro-2-aminodiphenylamine.

5-Amino-1 : 2-diphenylbenziminazole, prepared by reduction of the 5-nitro-base with zinc dust and alcoholic hydrogen chloride, forms an *acetyl* derivative,  $NHAc{\cdot}C_6H_3{<}\begin{matrix}\text{NPh}\\ \text{——N}\end{matrix}{>}CPh$, which crystallises in glistening needles and melts **at** 254°. G. Y.

[Hydroxynaphthiminazoles and their Azo-derivatives.] FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 172319).—The hydroxynaphthiminazoles having the general formula



$$CR{<}\begin{matrix}\text{N—}\\ \text{NR}^1\end{matrix}{>}C_{10}H_4{<}\begin{matrix}SO_3H(7)\\ OH(5)\end{matrix},$$

where R and R^1 are either hydrogen atoms or aliphatic or aromatic groups, are produced by the action of aldehydes or mixtures in molecular proportion of aldehydes and ketones, or of acid anhydrides or chlorides, on 5-hydroxy-1 : 2-naphthylenediamine-7-sulphonic acid. When acid anhydrides or chlorides are employed, the acyl derivative first obtained is heated with acids, when the iminazole ring is formed.

μ-Methyl-1 : 2-*naphthiminazole*-5-*hydroxy*-7-*sulphonic acid* is prepared by treating a neutral solution of 5-hydroxy-1 : 2-naphthylenediamine-7-sulphonic acid with acetic anhydride. When the solution no longer gives a coloration with sodium nitrite, it is heated to boiling and finally cooled, when the new compound crystallises out. By replacing acetic anhydride by benzoyl or *p*-nitrobenzoyl chloride in the foregoing condensation, 5-*hydroxy*-*μ*-*phenyl*-1 : 2-*naphthiminazole*-7-*sulphonic acid* and the corresponding p-*nitrophenyl* derivative are produced.

Phthalic anhydride may likewise be employed when *μ-carboxyphenyl*-1 : 2-*naphthiminazole*-5-*hydroxy*-7-*sulphonic acid* is formed.

G. T. M.

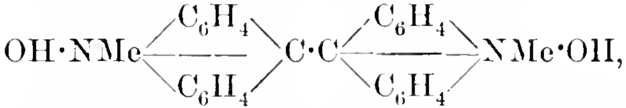
Molecular Weight of Indigotin. ERNST BECKMANN and WERNER GABEL (*Ber.*, 1906, 39, 2611—2618).—The authors have extended the experiments of Vaubel (Abstr., 1901, i, 714 ; 1902, i, 542) on the molecular weight of indigotin. Whilst Vaubel found, by the cryoscopic method with phenol and *p*-toluidine respectively, a molecular weight for indigotin corresponding with twice the value demanded by the Baeyer formula, the ebullioscopic determinations now quoted by the authors gave values corresponding with the single formula. The solvents used were quinoline, aniline, phenol, and *p*-toluidine.

The molecular rises of the boiling point of phenol and *p*-toluidine respectively were redetermined and found to be 34·40° and 41·40°.

Cryoscopic measurements with aniline and with phenol gave values corresponding with the single formula. Whilst the authors' results with phenol are at variance with Vaubel's, the results with *p*-toluidine agree. A. McK.

Molecular Weight of Indigotin. HERMANN WICHELHAUS (*Ber.*, 1906, **39**, 3298. Compare Beckmann and Gabel, preceding abstract).—The author draws attention to his determination of the molecular weight of *a*-naphthaleneindigo (Abstr., 1894, i, 42). G. Y.

Reduction of Cyclic Amine-ones. I. Preparation of Acridine from Acridone. HERMAN DECKER and GEORGES DUNANT (*Ber.*, 1906, **39**, 2720—2722).—When reduced with zinc and acetic acid, 10-methylacridone yields a mixture of a diacridyl derivative,



$$\mathrm{OH{\cdot}NMe}{<}\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}{>}\mathrm{C{\cdot}C}{<}\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}{>}\mathrm{NMe{\cdot}OH},$$

methylacridonium hydroxide, and methyldihydroacridine. The last is readily oxidised by 2 per cent. nitric acid to a methylacridonium nitrate.

As the acridonium salts are readily converted into acridine and methyl esters, these processes afford a convenient method for transforming acridone into acridine. J. J. S.

Action of Imino-ethers on Amino-esters. HERMANN FINGER and L. SCHUPP (*J. pr. Chem.*, 1906, [ii], **74**, 154).—4-Keto-2-phenyl-1 : 4-dihydroquinazoline, melting at 241°, is formed when a molecular mixture of benziminoethyl ether and methyl anthranilate is heated.

Imino-ethers condense in the same manner with *a*- and *β*-amino-esters of the fatty series. G. Y.

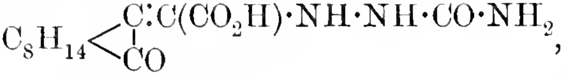
Diacridines. CARLO BAEZNER [in part with J. GUEORGUIEFF and AUGUST GARDIOL] (*Ber.*, 1906, **39**, 2650—2653. Compare this vol., i, 699, 887).—In the preparation of hydroxynaphthacridines by the reduction of *o*-nitrobenzyl chlorides with stannous chloride in the presence of dihydroxynaphthalenes, substances were obtained as by-products which were insoluble in alkali. These products became the main products of the action when the nitro-compound was used in the proportion of 2 mols. to 1 mol. of naphthol.

3′ : 3″-*Diamino*-2 : 7-*naphthalenediacridine*, $C_{24}H_{16}N_4$, is obtained from *o*-*p*-dinitrobenzyl chloride and 2 : 7-dihydroxynaphthalene, whilst 3′-amino-7-hydroxy-1 : 2-phenonaphthacridine is also obtained. The former separates from nitrobenzene in yellowish-red needles and decomposes at 360°. Its salts with mineral acids are highly coloured. Its *diacetyl* derivative separates from nitrobenzene in yellow needles and melts at 240—245°.

3′ : 3″-*Diamino*-2 : 3-*naphthalenediacridine*, $C_{24}H_{16}O_4$, obtained from *o*-*p*-dinitrobenzyl chloride and 2 : 3-dihydroxynaphthalene, separates from xylene in greyish-yellow needles. Its solution in concentrated sulphuric acid is yellow and exhibits bluish-green fluorescence. Its *hydrochloride* separates from dilute hydrochloric acid in violet-red crystals.

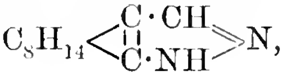
The reduction of *o*-nitrobenzyl chloride in presence of 2 : 7-dihydroxynaphthalene yielded, in addition to 7-hydroxy-1 : 2-phenonaphthacridine, a product insoluble in alkali but partly soluble in xylene. From the xylene solution a *compound* $C_{21}H_{18}ON_2$ was isolated; it melted at 123—125°. A. McK.

Action of Amines on Camphoroxalic Acid. J. BISHOP TINGLE and CHARLES J. ROBINSON (*Amer. Chem. J.*, 1906, **36**, 223—290).—By the action of semicarbazide on camphoroxalic acid, J. B. and A. Tingle (Abstr., 1900, i, 302) obtained a product which seemed to consist of two isomeric compounds of the composition



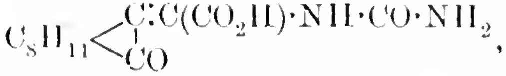
$$C_8H_{14}<\begin{array}{l}C{:}C(CO_2H)\cdot NH\cdot NH\cdot CO\cdot NH_2\\ |\\ CO\end{array},$$

which melted at 218° and 209—210° respectively. Tingle and Hoffman (Abstr., 1905, i, 800) obtained a similar compound which they termed semicarbazidocamphoformeneaminecarboxylic acid, which on crystallisation from alcohol melted at 200°, but when crystallised from glacial acetic acid melted at 209—210°. These experiments have been repeated and the apparently isomeric substances have been proved to be identical, the differences observed in the melting point being due to differences in the rate of heating. When camphoroxalic acid is heated with semicarbazide at 125° under pressure, hydrazodicarbamide and camphylpyrazolecarboxylic acid are obtained. The same compounds, together with camphyl-3-keto-1 : 2 : 4-heptatriazine, are produced when carbamylcamphoformeneaminecarboxylic acid (semicarbazidocamphoformeneaminecarboxylic acid) is heated at its melting point for twenty minutes.

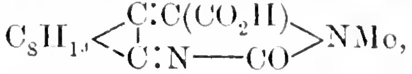
Camphylpyrazolecarboxylic acid,  $C_8H_{14}<\begin{array}{l}C\text{———}C\cdot CO_2H\\ \| \qquad\quad \|\\ C\cdot NH\cdot N\end{array}$, forms stout, colourless, prismatic crystals, melts at 255—258°, and is soluble in alcohol or acetone and slightly so in hot water. On fusion, it is converted into *camphylpyrazole*,  $C_8H_{14}<\begin{array}{l}C\cdot CH\\ \|\\ C\cdot NH\end{array}\!\!>N$, which remains unmelted at 288°.

Camphyl-3-keto-1 : 2 : 4-*heptatriazine*,  $C_8H_{14}<\begin{array}{l}C{:}CH\cdot NH\\ |\\ C{=\!=}N\cdot CO\end{array}\!\!>NH$, crystallises from alcohol in small, yellow prisms, melts at 305—306°, and is sparingly soluble in ether, acetone, benzene, or light petroleum.

Ethyl carbamylcamphoformeneaminecarboxylate (J. B. Tingle and A. Tingle, *loc. cit.*) melts at 191°, but the melting point varies with the rate of heating. If the ester is left in contact with the alcoholic hydrogen chloride solution in which it was produced, it undergoes decomposition with formation of *ethyl camphylpyrazolecarboxylate*, which crystallises from light petroleum in large, hemimorphic, monoclinic prisms and melts at 91—92°; its *hydrochloride* softens at 151° and melts at 156°.

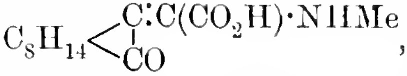
When an alcoholic solution of camphoroxalic acid and carbamide is heated under pressure at 135°, *formamidylcamphoformeneaminecarboxylic acid*,  $C_8H_{14}<\genfrac{}{}{0pt}{}{C:C(CO_2H)\cdot NH\cdot CO\cdot NH_2}{CO}$, is produced, which melts and decomposes at 192—194° and is readily soluble in alcohol and sparingly so in acetone, ethyl acetate, or chloroform.

Methylcarbamide reacts with camphoroxalic acid with formation of 2-*keto*-4 : 5-*camphyl*-1-*methylpyrimidine*-6-*carboxylic acid*,



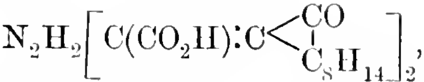
$$C_8H_{14}<\genfrac{}{}{0pt}{}{C:C(CO_2H)}{C:N\text{——}CO}>NMe,$$

which crystallises in long, pale yellow prisms, melts at 154°, and dissolves readily in ether, acetone, chloroform, or hot alcohol.

By the interaction of *s*-dimethylcarbamide and camphoroxalic acid, a small quantity of a *substance* melting at 104—105° is obtained, together with a larger amount of *methylcamphoformeneaminecarboxylic acid*,  $C_8H_{14}<\genfrac{}{}{0pt}{}{C:C(CO_2H)\cdot NHMe}{CO}$, which crystallises in long, colourless, prismatic needles, melts at 77—78°, and is very soluble in the usual organic solvents. Attempts were made to obtain condensation products of camphoroxalic acid and *as*-dimethylcarbamide, but without success.

Camphoroxalic acid reacts with a solution of hydrazine in methyl alcohol at the ordinary temperature with formation of hydrazine camphoroxalate, biscamphoformeneaminecarboxylic acid, and camphylpyrazolecarboxylic acid. *Hydrazine camphoroxalate*, $N_2H_4,2C_{12}H_{16}O_4$, is a pale yellow salt which begins to decompose at 186° and is completely melted at 245°.

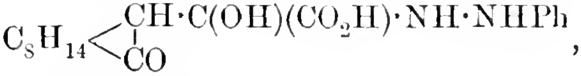
Biscamphoformeneaminecarboxylic acid,



$$N_2H_2\left[C(CO_2H):C<\genfrac{}{}{0pt}{}{CO}{C_8H_{14}}\right]_2,$$

crystallises in long, slender, pale yellow needles with 2 mols. of methyl alcohol, which it loses at 100° and becomes deep yellow; on further heating it begins to decompose at 137°, and is not completely melted at 155°. When the acid is heated at 150—155°, carbon dioxide is evolved and a product is obtained from which the following three substances were isolated. (1) A *compound*, $C_{24}H_{30}O_6N_2$, which crystallises in clusters of pale yellow needles, melts at 222—223° and has acid properties. (2) A *compound*, isomeric with the preceding substance, which has a dull yellow colour and melts at 232°; solutions of this compound gradually turn red and deposit red crystals which also melt at about 232°. (3) A *compound*, $C_{21}H_{30}O_5N_2$, which crystallises in light yellow prisms and melts at 221°.

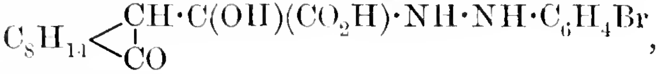
When phenylhydrazine (2 mols.) is added to camphoroxalic acid (1 mol.) in chloroform solution, the additive *compound*,



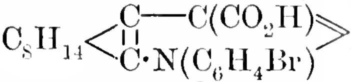
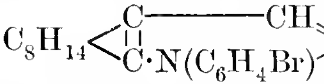
$$C_8H_{14}<\genfrac{}{}{0pt}{}{CH\cdot C(OH)(CO_2H)\cdot NH\cdot NHPh}{CO},$$

is produced, which crystallises in slender, yellow needles, melts at 120°, and is very stable. If the compound is fused or boiled with alcohol, it is converted into camphylphenylpyrazolecarboxylic acid (Abstr., 1897, i, 484), which melts at 196° and crystallises with 1 mol. of alcohol.

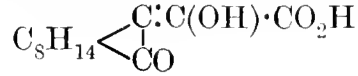
By the action of *p*-bromophenylhydrazine on camphoroxalic acid, there are produced (1) an additive *compound*,



$$C_8H_{14}<\begin{array}{l}CH\cdot C(OH)(CO_2H)\cdot NH\cdot NH\cdot C_6H_4Br\\ CO\end{array},$$

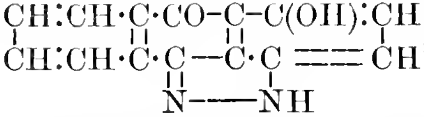
which crystallises in slender, yellow needles, melts at 149°, and is very stable, and (2) a *compound*, $C_{18}H_{21}O_3N_2Br$, which melts at 172°. When either of these substances is fused, *camphyl*-p-*bromophenylpyrazolecarboxylic acid*,  $C_8H_{14}<\begin{array}{l}C\text{——}C(CO_2H)\\ C\cdot N(C_6H_4Br)\end{array}>N$, is produced which crystallises from benzene in clusters of minute, colourless needles and melts at 215°; the *ethyl* ester separates from acetone in triclinic crystals, melts at 149°, and, unlike ethyl camphylpyrazolecarboxylate, does not possess basic properties. When this acid is heated at its melting point, carbon dioxide is evolved, and a compound, probably *camphyl*-p-*bromophenylpyrazole*,  $C_8H_{14}<\begin{array}{l}C\text{————}CH\\ C\cdot N(C_6H_4Br)\end{array}>N$, is obtained, which is very soluble in the ordinary organic solvents and, on evaporating its solutions, remains as a gummy mass.

On investigating the hydration product of camphoroxalic acid (Abstr., 1898, i, 443), evidence was obtained that the water is not present as water of crystallisation. The hydration product reacts with aniline and with semicarbazide with formation of substances identical with those obtained from the acid itself. With hydroxylamine, the hydration product yields a *substance* which melts at 181—182°.

A table is given showing the relations between the various derivatives of camphoroxalic acid which have been obtained by the action of amines, and a summary is made of the various facts which support the conclusion that camphoroxalic acid has the keto-enolic structure represented by the formula  $C_8H_{14}<\begin{array}{l}C{:}C(OH)\cdot CO_2H\\ CO\end{array}$. E. G.

Preparation of Pyrazoles from Anthraquinone Derivatives.

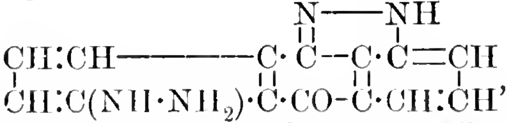
Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 171293).—The *pyrazole* derivative,



$$\begin{array}{l}CH{:}CH\cdot C\cdot CO\text{—}C\text{—}C(OH){:}CH\\ CH{:}CH\cdot C\cdot C\text{—}C\cdot C\equiv CH\\ \qquad\qquad N\text{——}NH\end{array},$$

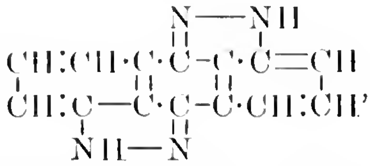
is produced by heating 4-hydrazino-1-hydroxyanthraquinone hydrochloride with aniline and aniline hydrochloride at 170—180°. At first a molecular compound of the substance with aniline is obtained, but the base is removed on washing with solvents. This pyrazole derivative dissolves in concentrated sulphuric acid or aqueous sodium hydroxide to a yellow solution having an intense green fluorescence.

The *monopyrazole* derivative,



$$\begin{array}{l}\qquad\qquad\qquad\qquad N\text{——}NH\\ CH{:}CH\text{————}C\cdot C\text{—}C\cdot C\equiv CH\\ CH{:}C(NH\cdot NH_2)\cdot C\cdot CO\text{—}C\cdot CH{:}CH\end{array},$$

is prepared by boiling a slightly acidified aqueous solution of dihydrazinoanthraquinone hydrochloride, when the product separates in graphitic crystals. The *dipyrazole* derivative,



$$\begin{array}{c} \mathrm{N{-\!-}NH} \\ \mathrm{CH{:}CH{\cdot}C{\cdot}C{-}C{\cdot}C{=}CH} \\ \mathrm{CH{:}C{-\!-}C{\cdot}C{-}C{\cdot}CH{:}CH} \\ \mathrm{NH{-\!-}N} \end{array}$$

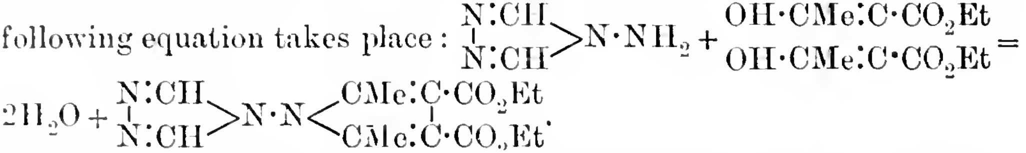
is formed when 1 : 5-disulphohydrazinoanthraquinone is heated at 140° with 3—5 per cent. hydrochloric acid. The product separates as its crystalline hydrochloride, and the base, which, when first set free, is amorphous, gradually assumes a crystalline form and is soluble in dilute aqueous sodium hydroxide to a yellow solution with a green fluorescence. Its solution in concentrated sulphuric acid is colourless, but has an intense blue fluorescence. G. T. M.

Preparation of Azines of the Anthraquinone Series. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 170562).—The *o*-diamines of the anthraquinone series, when condensed with *o*-diketones, furnish azines having the valuable property of dyeing unmordanted cotton. The *azine*, $\begin{array}{l}\mathrm{CH{:}CH{\cdot}C{\cdot}CO{\cdot}C{\cdot}CH{:}C{\cdot}N{:}C{\cdot}C_6H_4} \\ \mathrm{CH{:}CH{\cdot}C{\cdot}CO{\cdot}C{\cdot}CH{:}C{\cdot}N{:}C{-\!-}CH}\end{array}\!\!>\!\mathrm{CH}$, obtained by condensing 2:3-diaminoanthraquinone and β-naphthaquinone in boiling glacial acetic acid, separates in needles and in the reducing vat produces yellow shades on cotton. Similar *azines* were produced from 2 : 3-diaminoanthraquinone with phenanthraquinone, β-anthraquinone, and the oxidation product of alizarin-blue. 1 : 2-Diaminoanthraquinone also gives rise to an azine with β-naphthaquinone, whilst two products are obtained on condensing it with β-anthraquinone. G. T. M.

Constitution of *iso*Rosindone and Allied Substances. Herman Decker and August Würsch (*Ber.*, 1906, **39**, 2653—2656).—The inactivity of *iso*rosindone towards magnesium phenyl bromide is an argument in favour of the phenolbetaine formula. The substance is unimolecular in benzene solution. C. S.

1-Amino-3 : 4-triazole (*N*-Amino-$\beta\beta'$-pyrrodiazole). A Contribution to the Knowledge of the so-called "*N*-Dihydrotetrazine" (*iso*Bisdiazomethane, Trimethinetriazoimide). Carl Bülow (*Ber.*, 1906, **39**, 2618—2622).—The compound described by Curtius and Lang as trimethinetriazoimide and by Hantzsch and Silberrad as dihydrotetrazine, $\mathrm{CH}\!<\!\begin{array}{c}\mathrm{NH{\cdot}N}\\ \mathrm{N{\cdot}NH}\end{array}\!\!>\!\mathrm{CH}$, is considered by the author to be 1-amino-3 : 4-triazole, $\mathrm{NH_2{\cdot}N}\!<\!\begin{array}{l}\mathrm{CH{:}N}\\ \mathrm{CH{:}N}\end{array}$. The behaviour of the compound was not in satisfactory accord with the formulæ advanced by previous authors. The new formula, however, is not contradictory to the fact that the compound yields a monoacetyl derivative only and not a diacetyl one, since it would be expected that the salts formed would undergo hydrolysis. Again, the formula accords with the formation of a 1 : 3 : 4-triazole by the action of nitrous acid. Further, the formation of condensation products with aldehydes is readily accounted for.

A direct proof that the so-called dihydrotetrazine is in reality 1-amino-3 : 4-triazole is afforded by its comportment with ethyl diacetylsuccinate (compare Bülow, Abstr., 1903, i, 196; Bülow and Sautermeister, Abstr., 1904, i, 690), when the action represented by the following equation takes place :



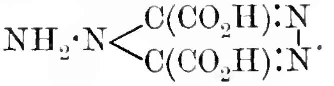
$$\begin{array}{l}N{:}CH\\ N{:}CH\end{array}\!\!>N\cdot NH_2+\begin{array}{l}OH\cdot CMe{:}C\cdot CO_2Et\\ OH\cdot CMe{:}C\cdot CO_2Et\end{array}=2H_2O+\begin{array}{l}N{:}CH\\ N{:}CH\end{array}\!\!>N\cdot N\!\!<\begin{array}{l}CMe{:}C\cdot CO_2Et\\ CMe{:}C\cdot CO_2Et\end{array}.$$

Ethyl 1 : 1-*triazole*-2 : 5-*dimethylpyrrole*-3 : 4-*dicarboxylate*, prepared in the manner indicated, crystallises from water in needles and melts at 146—147°.

It follows that Hantzsch and Silberrad's *N*-dihydrotetrazinedicarboxylic acid,

$$CO_2H\cdot C\!\!<\begin{array}{l}N\cdot NH\\ NH\cdot N\end{array}\!\!>C\cdot CO_2H,$$

is 1-amino-3 : 4-triazole-2 : 5-carboxylic acid,



$$NH_2\cdot N\!\!<\begin{array}{l}C(CO_2H){:}N\\ C(CO_2H){:}N\end{array}.$$

A. McK.

[*p*-Aminophenylnaphthyl-1 : 2-triazole-3 : 8-disulphonic Acid.] Aktien-Gesellschaft für Anilin-Fabrikation (D.R.-P. 170513).—p-*Aminophenylnaphthyl*-1 : 2-*triazole*-3 : 8-*disulphonic acid*,

$$C_{10}H_4(HSO_3)_2\!\!<\begin{array}{c}N\\ |\\ N\end{array}\!\!>N\cdot C_6H_4\cdot NH_2,$$

is obtained by successively condensing α-naphthylamine-3 : 8-sulphonic acid with diazotised *p*-nitroaniline, oxidising the azo-compound thus formed to the corresponding nitrotriazole derivative, and then reducing the nitro-group with acid or alkaline reducing agents.

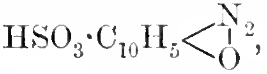
This aminotriazolesulphonic acid, when diazotised and combined with β-naphthol-3 : 6-disulphonic acid, furnishes a useful violet, lake-forming azo-derivative. G. T. M.

Diazobenzene Perchlorate and Phenylacridine Perchlorate Daniel Vorländer (*Ber.*, 1906, 39, 2713—2715).—10-Phenylacridine dissolved in dilute 2—3 per cent. sulphuric acid gives with a dilute solution of perchloric acid (1 in 100) a voluminous precipitate of phenylacridine perchlorate consisting of slender, yellow needles. With a more dilute solution (1 in 1000) a turbidity is first produced, and then long, yellow needles separate. Chloric and hypochlorous acids do not yield precipitates except in more concentrated solutions. The test for perchloric acid is not conclusive, since a few acids, nitric acid in particular, form sparingly soluble salts of phenylacridine.

Diazobenzene perchlorate, $C_6H_5\cdot N_2\cdot ClO_4$, separates in white needles when aniline is diazotised in perchloric acid solution, or when a 10 per cent. solution of diazobenzene chloride is treated with perchloric acid. It explodes even in the wet state, but remains white in the cold for one day.

The diazonium perchlorates obtained from *p*-toluidine, *p*-nitroaniline, *o*-, *m*-, and *p*-chloroaniline, *p*-bromoaniline, *o*-, *m*-, and *p*-aminobenzoic acid, *o*- and *p*-anisidine, and benzidine have been prepared. The para-compounds are the least unstable. C. S.

Diazonium Perchlorates. KARL A. HOFMANN and H. ARNOLDI (*Ber.*, 1906, 39, 3146—3148).—*Diazobenzene perchlorate*, $C_6H_5\cdot N_2\cdot ClO_4$, prepared by diazotising an aqueous solution of aniline in a mixture of hydrochloric and perchloric acids, is sparingly soluble in water and is a very violent explosive. Compounds with similar explosive properties were obtained from *o*-toluidine, *p*-toluidine, α-naphthylamine, and β-naphthylamine respectively. A. McK.

Preparation of Diazo-oxynaphthalenesulphonic Acids and their Anhydrides. ANILINFARBEN- & EXTRACT-FABRIKEN VORM. J. R. GEIGY (D.R.-P. 171024).—The *o*-aminonaphthols and their sulphonic acids are not readily diazotised by the ordinary process, oxidation occurs, and β-naphthaquinone derivatives may be formed. This result occurs to some extent even in the absence of mineral acid, and is increased on warming the solution. It has now been ascertained that the addition of a comparatively small amount of a cupric salt renders the diazotisation of the aminonaphtholsulphonic acid complete even in the absence of mineral acid, and at the same time reduces the oxidising action to a minimum. To a well-cooled thin paste of 1-amino-β-naphthol-4-sulphonic acid were added successively cold concentrated solutions of copper sulphate and sodium nitrite. The diazotisation proceeded quite smoothly, the product being soluble and yielding an orange-yellow solution from which 1-*diazo-2-oxynaphthalene-4-sulphonic acid*,  $HSO_3\cdot C_{10}H_5<\begin{matrix}N_2\\|\\O\end{matrix}$, separated in fine yellow needles on the addition of concentrated hydrochloric acid. This diazo-compound, which is not explosive when dry, combines with resorcinol to furnish a dark violet azo-derivative.

Barium-1-*diazo*-2-*oxynaphthalene*-6-*sulphonate* was obtained as a golden-yellow, crystalline precipitate on adding successively copper chloride, sodium nitrite, hydrochloric acid, and barium chloride to a cold aqueous solution of 1-amino-β-naphthol-6-sulphonic acid. *Barium*-1-*diazo*-2-*oxynaphthalene*-7-*sulphonate*, a light brown, crystalline substance, was prepared in a similar manner.

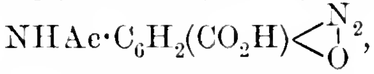
1-*Diazo*-2-*oxynaphthalene*-8-*sulphonic acid*, produced from the corresponding 1-amino-β-naphthol-8-sulphonic acid, separates in colourless needles with a silvery lustre; this substance condenses with the phenols only with some difficulty; in the case of alkaline resorcinol, the solution has to be strongly heated.

The diazo-oxides of the 1-amino-β-naphtholdisulphonic acids were also prepared through the agency of a cupric salt, and were isolated either as alkali or barium salts, and 1-*diazo*-2-*oxynaphthalene*-3 : 6 : 8-*trisulphonic acid* was obtained in the form of its crystalline, orange-yellow acid *sodium* salt.

In some cases a ferrous salt was employed instead of the copper compound. The mono-, di-, and tri-sulphonic acids of 2-amino-α-naphthol were also diazotised in this way, and were usually isolated in the form of the crystalline, yellow sodium salts. The patent contains a tabulated description of seventeen new diazo-oxynaphthalene sulphonic acids. G. T. M.

Preparation of the Anhydrides of 1-Diazo-2-hydroxy- and 2-Diazo-1-hydroxy-naphthalenes. Anilinfarben- & Extract-fabriken vorm. J. R. Geigy (D.R.-P. 172446. Compare preceding abstract).—1-Amino-β-naphthol and 2-amino-α-naphthol can both be readily diazotised by treating the aqueous solutions of their hydrochlorides with a dilute solution of sodium nitrite and copper sulphate. 1-Diazo-2-oxynaphthalene, $C_{10}H_6<\overset{N_2}{\underset{O}{|}}$, is precipitated in yellow crystals on the addition of sodium chloride, whilst the crude 2-*diazo-1-oxynaphthalene* separates in yellowish-green crystals which are redissolved in the solution at 80°, and reprecipitated in yellow crystals on cooling. These compounds are very sensitive to light, darkening rapidly even in diffused daylight. G. T. M.

Azo-derivatives of 3-Amino-5-acetylaminosalicylic Acid. Leopold Cassella & Co. (D.R.-P. 170819).—3-*Amino-5-acetylaminosalicylic acid*, $OH\cdot C_6H_2(NH_2)(NHAc)\cdot CO_2H$, which is obtained by successively nitrating and reducing acetyl-*p*-aminosalicylic acid, yields on diazotisation a sparingly soluble golden-yellow diazo-derivative,



$$NHAc\cdot C_6H_2(CO_2H)<\overset{N_2}{\underset{O}{|}},$$

which combines with the sulphonic acids of the naphthols and dihydroxynaphthalenes to furnish a series of valuable mordant dyeing colouring matters. G. T. M.

***para*-Substituted *o*-Nitrobenzaldehydes. V.** Franz Sachs and Hermann Kantorowicz (*Ber.*, 1906, **39**, 2754—2762. Compare Abstr., 1902, i, 377, 682; 1903, i, 425; 1904, i, 62, 506, 593; 1905, i, 202; this vol., i, 575).—2-*Nitrobenzaldehyde-4-diazonium sulphate*, $CHO\cdot C_6H_3(NO_2)\cdot N_2\cdot SO_4H$, obtained by the action of amyl nitrite and sulphuric acid on 2-nitro-4-aminobenzaldoxime, is a pale yellow solid, readily soluble in water, but insoluble in most organic solvents, and decomposes when exposed to the air. The corresponding *chloride*, $C_7H_4O_3N_3Cl$, is more explosive and also more reactive.

Dimethylaniline-p-*azo*-o-*nitrobenzaldehyde*,

$$NMe_2\cdot C_6H_4\cdot N_2\cdot C_6H_3(NO_2)\cdot CHO,$$

obtained by coupling the chloride with an acetic acid solution of dimethylaniline, crystallises in bordeaux-red, glistening plates and melts at 219—220°. It dissolves readily in most organic solvents, but only sparingly in water, and readily dyes silk or wool. The *phenylhydrazone* gives a deeper shade of colour and is faster. *Naphthol*-p-*azo*-o-*nitrobenzaldehyde*, $OH\cdot C_{10}H_6\cdot N_2\cdot C_6H_3(NO_2)\cdot CHO$, crystallises from acetic acid, melts at 208°, and is only sparingly soluble in water. *Phenol*-p-*azo*-o-*nitrobenzaldehyde*, $OH\cdot C_6H_4\cdot N_2\cdot C_6H_3(NO_2)\cdot CHO$, melts at 162°, dyes wool or silk rose-red, and yields a *phenylhydrazone*. 4-*Iodo-2-nitrobenzaldehyde*, $NO_2\cdot C_6H_3I\cdot CHO$, melts at 112° and resembles the corresponding chloro- and bromo-compounds, but is far less stable, and, after exposure to sunlight for several hours is transformed into iodonitrosobenzoic acid. The *phenylhydrazone*,

$$NO_2\cdot C_6H_3I\cdot CH:N_2HPh,$$

crystallises from alcohol in red needles melting at 185°, and the *semicarbazone*, $C_8H_7O_3N_4I$, from acetic acid in pale yellow, rectangular plates, which melt and decompose at 284°.

2-*Nitro-4-hydroxybenzaldehyde*, $NO_2\cdot C_6H_3(OH)\cdot CHO$, obtained by decomposing the diazonium salts, crystallises from alcohol in yellow needles melting at 67° and has an intense odour. The *phenylhydrazone*, $C_{13}H_{11}O_3N_3$, forms glistening, red needles and melts at 189—190°.

2 : 4-*Dinitrobenzaldehyde*-p-*bromophenylhydrazone* forms red crystals melting at 226—227°, and its alcoholic solution gives a characteristic blue colour on the addition of a drop of potassium hydroxide solution. The corresponding *phenylmethylhydrazone*, $C_{11}H_{12}O_4N_4$, forms purple-red crystals melting at 194°.

2 : 4 : 6-*Trinitrobenzaldehyde*-p-*bromophenylhydrazone*, $C_{13}H_8O_6N_5Br$, crystallises from acetic acid in glistening, reddish-brown prisms melting at 242°. *Trinitrobenzaldehydephenylhydrazone*-p-*sulphonic acid*,

$$C_6H_2(NO_2)_3\cdot CH{:}N_2H\cdot C_6H_4\cdot SO_3H,$$

crystallises in pale red needles melting at 211°. It dissolves in alcohol and also in hot water, the aqueous solution giving brilliant but unstable colours with potassium hydroxide. Trinitrobenzaldehyde combines with sodium hydrogen sulphite and also yields a *semicarbazone*, $C_8H_6O_7N_6$, in the form of pale yellow plates melting at 214°. *Trinitrobenzylidenebenzidine*, $C_6H_2(NO_2)_3\cdot CH{:}N\cdot C_{12}H_8\cdot NH_2$, crystallises from xylene or amyl alcohol in glistening, blood-red plates melting at 223° and readily soluble in acetone or nitrobenzene. *Trinitrobenzylideneaniline*, $C_{13}H_8O_6N_4$, crystallises in reddish-yellow needles melting at 162°.

When reduced with alcoholic ammonium sulphide, the trinitroaldehyde yields an extremely unstable pale yellow compound.

2 : 6-*Dinitro-4-aminobenzaldehydephenylhydrazone*, $C_{13}H_{11}O_4N_5$, obtained by the action of phenylhydrazine on the oxime, melts at 250°.

2 : 6-*Dinitrobenzaldehyde-4-diazonium chloride*, $C_7H_3O_5N_4Cl$, is readily soluble in water, and explodes violently when heated. The azo-derivatives of *o*-nitrobenzaldehyde do not yield indigo dyes with acetone and alkali.

J. J. S.

Azo-colouring Matters of the Pyridine Series. R. BAUMERT (*Ber.*, 1906, **39**, 2971—2976).—Azo-colouring matters containing the pyridine ring have not hitherto been obtained, but by diazotising *p*-amino-4-stilbazole and *p*-amino-2-stilbazole, and coupling the products with phenols and amines, compounds of this kind have now been obtained.

p-*Nitro-4-stilbazole*, $C_5NH_4\cdot CH{:}CH\cdot C_6H_4\cdot NO_2$, prepared by heating approximately equal weights of γ-picoline, *p*-nitrobenzaldehyde, and freshly melted zinc chloride for nine hours at 150—160°, was obtained in the form of brown crusts after removing unaltered γ-picoline by distillation in steam; it forms yellow needles melting at 118—119°, is almost insoluble in water, and dissolves readily in organic media. Its crystalline *hydrochloride* melts at 257—258°; the *platini-* and *aurichlorides* are also crystalline.

p-*Amino-2-stilbazole*, obtained by reducing *p*-nitro-2-stilbazole, crystallises from dilute alcohol in pale yellow needles melting at 138—139°;

its *stannochloride*, $C_{13}H_{14}N_2Cl_2,2SnCl_2$, obtained during the reduction, melts at 198—199°; the *platinichloride* forms yellow needles.

Di-2-stilbazylthiocarbamide, $C_{27}H_{22}N_4S$, which results from the condensation of *p*-amino-2-stilbazole and carbon disulphide in alcoholic potash, melts at 180—181° and forms a yellow *platinichloride*, $C_{27}H_{22}N_4S(H_2PtCl_6)_2$. *Acetyl*-p-*amino-2-stilbazole*, $C_{15}H_{14}ON_2$, crystallises from dilute alcohol in slender needles and melts at 170—171°.

p-*Amino-4-stilbazole*, prepared by reducing *p*-nitro-4-stilbazole, melts at 138—139°; its *hydrochloride* and *stannochloride*, $C_{13}H_{14}N_2Cl_2.2SnCl_2$, melt at 257—258° and 198—199° respectively; the *platinichloride* melts above 300°. The *thiocarbamide* derivative melts at 195—196°; its *platinichloride* melts above 300°.

2-Stilbazole-p-*azo-β-naphthol hydrochloride*,

$$HO\cdot C_{10}H_6\cdot N_2\cdot C_6H_4\cdot CH\colon CH\cdot C_5NH_4,HCl,$$

was obtained by adding a solution of diazotised *p*-amino-2-stilbazole to alkaline β-naphthol and subsequently acidifying the solution of the azo-compound. This salt, which crystallises from 90 per cent. alcohol in reddish-brown leaflets, melts at 252—253° and dyes silk, wool, and ordinary and mordanted cotton; it is only slightly soluble in water, and, like benzeneazo-β-naphthol, is devoid of phenolic properties, being insoluble in aqueous alkali hydroxides.

4-Stilbazole-p-*azo-β-naphthol hydrochloride* resembles its isomeride, but dyes in somewhat deeper shades and melts at 257—258°.

The hydrochlorides of *2-stilbazole*-p-*azoresorcinol* and *4 stilbazole*-p-*azoresorcinol* are brown powders sparingly soluble in water, more so in alcohol, and dissolving in aqueous alkali hydroxides.

Sodium 2-stilbazole-p-*azo-β-naphthol-6-sulphonate*,

$$NaSO_3\cdot C_{10}H_5(OH)\cdot N_2\cdot C_6H_4\cdot CH\colon CH\cdot C_5NH_4,$$

crystallises from 90 per cent. alcohol in needles having a green, metallic lustre; its isomeride from diazo-4-stilbazole has similar properties. Similar dyes can be obtained from the two isomeric diazostilbazoles with β-naphthol-3 : 6-disulphonic acid and also with β-naphthol-6 : 8-disulphonic acid, salicylic acid, dimethylaniline, and sulphanilic acid.

G. T. M.

Tertiary Aromatic Amines. V. CARL HAEUSSERMANN (*Ber.*, 1906, 39, 2762—2765).—*Tetraphenyldiaminoazobenzene*, $C_{36}H_{28}N_4$, is obtained when nitrotriphenylamine is reduced electrolytically. The best results are obtained when the cathode compartment contains an alcoholic solution of the nitro-compound and sodium acetate, the anode compartment an aqueous solution of sodium hydroxide, and the electrodes are of nickel gauze or platinum.

The azo-compound separates from benzene as orange-red crystals melting at 201—202·5°, and is only sparingly soluble in alcohol or acetone.

Aminotriphenylamine (Herz, Abstr., 1890, 1409), obtained by the action of ammonia on its hydrochloride, crystallises from ether or alcohol in glistening, colourless needles melting at 146—147·5° and distilling above 360°.

Triphenylamine does not readily condense with diazobenzene chloride, whereas diphenyl-*m*-toluidine reacts with an acetic acid solution of diazobenzene chloride, yielding *benzeneazodiphenyl-m-toluidine*, $C_{25}H_{21}N_3$, which, after repeated crystallisation from acetone, forms scarlet-red needles melting at 168—169°. It is readily soluble in benzene, but less so in alcohol.

Triphenylamine and benzaldehyde condense in the presence of 50 per cent. sulphuric acid, yielding a pale green product which, after extraction with alcohol, is colourless. It probably consists of tetraphenyldiaminotriphenylmethane. J. J. S.

Azimino-compounds from Aromatic *para*-Diamines.

GILBERT T. MORGAN and FRANCES M. G. MICKLETHWAIT (*Ber.*, 1906, **39**, 2869—2875. Compare Trans., 1905, **87**, 73; 1906, **89**, 1158).—*p*-Toluenesulphonyl-5-nitro-*o*-toluidine (Reverdin and Crépieux, Abstr., 1902, i, 238, 434) may be obtained by the action of *p*-toluenesulphonic chloride on a boiling toluene solution of 5-nitro-*o*-toluidine; when reduced with iron filings and dilute acetic acid, it yields p-*toluenesulphonyl*-p-*toluenyldiamine*, $NH_2\cdot C_6H_3Me\cdot NH\cdot SO_2\cdot C_7H_7$
$[NH_2 : Me : NH = 1 : 3 : 4]$,
which crystallises from dilute alcohol in slender prisms melting at 150°. When the diazonium chloride derived from the base is mixed with excess of sodium acetate solution, it yields p-*toluenesulphonyl*-p-*aziminotoluene*,  $C_6H_3Me{<}\begin{matrix}N\cdot SO_2\cdot C_7H_7\\ | \\ N_2\end{matrix}$; this is practically insoluble in the usual organic solvents, but dissolves sparingly in hot pyridine, naphthalene, or *p*-toluidine. It has a pale yellow colour and decomposes violently at 156°. The azimino-compound is converted back into the diazonium salt by cold concentrated hydrochloric acid and then condenses with β-naphthol, yielding 2-p-*toluenesulphonylaminotoluene*-5-*azo*-β-*naphthol*, $OH\cdot C_{10}H_6\cdot N_2\cdot C_6H_3Me\cdot NH\cdot SO_2\cdot C_7H_7$, which crystallises from benzene or acetic acid in glistening, red needles melting at 194°.

The same azo-compound can be obtained by heating equivalent quantities of the azimino-compound and β-naphthol in dry pyridine.

p-*Toluenesulphonylmethyl-5-nitro-o-toluidine*,
$NO_2\cdot C_6H_3Me\cdot NMe\cdot SO_2\cdot C_6H_4Me$,
obtained by heating Reverdin and Crépieux's nitro-compound with methyl iodide and alkali in methyl-alcoholic solution, melts at 103—105°. When reduced it yields p-*toluenesulphonylmethyl*-p-*toluenediamine*, $NH_2\cdot C_6H_3Me\cdot NMe\cdot SO_2\cdot C_7H_7$, which crystallises in colourless plates melting at 118—119°; the corresponding diazonium salt does not yield an azimino-compound with sodium acetate, but couples with β-naphthol to an *azo-dye*, $C_{25}H_{23}O_3N_3S$, which separates from acetic acid in deep red, nodular crystals melting at 181°. J. J. S.

Condensation of Diazobenzeneimides with Pyrazolones.

REINHOLD VON WALTHER and P. ROTHACKER (*J. pr. Chem.*, 1906, [ii], **74**, 207—208. Compare Dimroth, Abstr., 1902, i, 403).—The action of various diazobenzeneimides on phenylmethylpyrazolone in presence of sodium ethoxide leads to the formation of a red *product*, which is formed also in small quantities by the interaction of 4-dichloropyrazolone, pyrazolone, and hydrazine. It melts at 184°, is insoluble in water, only sparingly so in organic solvents, is readily soluble in hot dilute alkali hydroxides or concentrated sulphuric or hydrochloric acid, and forms two series of salts, of which the acid series is yellowish- to blood-red, whilst the normal salts are yellow, and are readily soluble in water, alcohol, or ether; the *platinichloride* can be extracted from its aqueous solution by shaking with ether. The *acetyl* derivative is yellow to dark red, the diacetyl derivative is yellow. The decomposition of the product melting at 184° leads to the formation on the one hand of rubazonic acid and bispyrazolone, and on the other of hydrazine; it contains probably 2 mols. of the pyrazolone coupled by means of a hydrazine group.

1-Phenyl-3:4-dimethylpyrazolone does not react with diazobenzeneimide. G. Y.

Production of Colloidal Preparations containing Gold, Silver, or Copper.

KALLE & Co. (D.R.-P. 170433, 170434).—Colloidal substances containing silver or gold are obtained by adding silver nitrate or gold chloride to an alkaline solution of the alkali salts of the fission products of albumin (lysalbinates, protoalbinates, alkali albumoses, &c.), warming gently for some time, and then dialysing the solution. The colloidal solution thus obtained yields a precipitate with dilute acid which may be again dissolved in alkali and purified by repeated dialysis.

An alkaline solution containing sodium protoalbinate, sodium hydroxide, and copper sulphate, when dialysed until the diffusate was neutral and then evaporated on the water-bath, furnished a brownish-black powder containing 18—19 per cent. of copper, which dissolves in water and aqueous sodium hydroxide to brown and violet solutions respectively. The other fission products of albumin gave rise to similar copper compounds. G. T. M.

Equilibrium between Proteids and Electrolytes. III. Solubility of Globulin in Magnesium Sulphate: Influence of Temperature.

GINO GALEOTTI (*Zeit. physiol. Chem.*, 1906, **48**, 473—480. Compare Abstr., 1905, ii, 512).—The more concentrated a solution of magnesium sulphate is, the more serum-globulin does it dissolve. When the concentration approaches saturation, the globulin is precipitated, and this precipitation depends on the concentration. The term fractional globulin precipitation should not be used if that expression means that the globulins in the fractions are distinct substances. An increase of temperature increases the solubility of the globulin in dilute solutions of the salt, but lessens it in concentrated solutions. W. D. H.

Hydrolysis of Vitellin.

EMIL ABDERHALDEN and ANDREW HUNTER (*Zeit. physiol. Chem.*, 1906, **48**, 505—512).—The following figures relate to the monoamino-acids of vitellin from egg yolk, compared with those similarly obtained by hydrolysis from the closely related proteid caseinogen of cow's milk. The numbers given are percentages.

	Vitellin.	Caseinogen.
Glycine	1·1	0
Alanine	present	0·9
Aminovaleric acid	2·4	1·0
Leucine	11·0	10·5
Aspartic acid	0·5	1·2
Glutamic acid	12·2	11·0
Phenylalanine	2·8	3·2
Proline	3·3	3·1
Serine	—	0·23
Tyrosine	1·6	4·5

W. D. H.

Cleavage Products of Vitellin. Phoebus A. Levene and C. L. Alsberg (*J. Biol. Chem.*, 1906, 2, 127—133).—One hundred grams of vitellin yield, glycine, traces; alanine, 0·16; leucine, 3·3; proline, 4; aspartic acid, 0·6; glutamic acid, 1; phenylalanine, 1; tyrosine, 0·4; histidine, traces; arginine, 1·2; and lysine, 2·4. The high proportion of proline [pyrrolidine-2-carboxylic acid] is significant in view of the fact that vitellin furnishes the material for the production of hæmoglobin. W. D. H.

Deaminocasein. Zdenko H. Skraup and Ph. Hoernes (*Monatsh.*, 1906, 27, 631—652. Compare Paal, Abstr., 1896, i, 455; Schiff, *ibid.*, 632; Schroetter, Abstr., 1898, i, 610).—The action of sodium nitrite on casein dissolved in glacial acetic acid at the ordinary temperature and finally on the water-bath leads to the formation of *deaminocasein*, $C_{216}H_{349}O_{78}N_{54}SP_{0\cdot4}$; it is obtained as a light yellowish-brown substance, does not give Millon's or the biuret reaction, is much less soluble than is casein in aqueous alkali hydroxides or acids, gives Liebermann's nitroso-reaction, and forms a brown, gelatinous *sodium* derivative. When hydrolysed with boiling 36 per cent. sulphuric acid it yields oxalic acid; the product of the hydrolysis with fuming hydrochloric acid, when treated according to Fischer's method (Abstr., 1901, i, 780), is found to contain leucine, aminovaleric acid, pyrrolidine-2-carboxylic acid, and probably glycine and *iso*leucine; glutamic, caseic, and caseanic acids are present in about the same amounts as, but arginine in much smaller quantity than, in the hydrolysis products of casein. Lysine and tyrosine are not present, whilst the presence of alanine is doubtful.

When boiled with dilute sulphuric acid, casein yields 1·38, deaminocasin 1·77 per cent. of ammonia. G. Y.

Deaminoglutin. Zdenko H. Skraup (*Monatsh.*, 1906, 27, 653—662. Compare Skraup and Hoernes, preceding abstract).—*Deaminoglutin*, $C_{1039}H_{1669}O_{391}N_{297}S$ or, omitting consideration of the sulphur, $C_{3\cdot51}H_{5\cdot71}O_{1\cdot32}N$ (glutin, $C_{3\cdot23}H_{5\cdot31}O_{1\cdot27}N$), is prepared by treating gelatin with sodium nitrite in acetic acid solution; it forms a light brownish-yellow resin, is readily soluble in water, less so in alcohol, gives a reddish-violet biuret reaction, and when hydrolysed by means of fuming hydrochloric acid on the water-bath, forms a fluorescent solution. The product of hydrolysis contains oxalic acid, glycine, histidine, and arginine. Lysine, which is present as a product of the hydrolysis of glutin, is not obtained from deaminoglutin; in its place there is found a *picrate* which melts at 149—150° and yields a product melting at about 220°, together with a hydroxyaminovaleric acid crystallising in leaflets, and melting at 252°. The *picrate* formed from this gives analytical results agreeing best with those required by the picrate of an aminovaleric acid, $C_{11}H_{14}O_9N_4$. G. Y.

Monoamino-acids of Gluten. Emil Abderhalden and Fernand Malengreau (*Zeit. physiol. Chem.*, 1906, **48**, 513—518).—The following figures are the percentages of amino-acids obtained from gliadin, the proteid of gluten of wheat which is soluble in alcohol, compared with those from gluten (or gluten-casein) which is insoluble in that reagent.

	Gluten.	Gliadin.
Glycine	0·41	0·68
Alanine	0·3	2·66
Aminovaleric acid	not found	0·33
Leucine	4·1	6·0
Proline	3·97	2·4
Glutamic acid	24·0	31·5
Aspartic acid	0·64	1·24
Phenylalanine	1·0	2·6
Tyrosine	1·9	2·37
Tryptophan	not estimated.	1·0 (approx.)
Serine		0·12
Lysine	2·15	0·0
Histidine	1·16	1·2
Arginine	4·4	2·75

W. D. H.

Formation of Methæmoglobin. II. Allexis Babel (*Arch. Sci. phys. nat.*, 1906, [iv], **22**, 216—239).—The substances (compare this vol., i, 779) which convert oxyhæmoglobin into methæmoglobin are not acting as catalytic agents, because if care is taken to avoid secondary reactions it is not possible to recover the whole of the substance at the end of the reaction; and, further, there exists for each substance a limiting quantity below which it is incapable of effecting any change in the oxyhæmoglobin. It is probable that in the conversion of oxyhæmoglobin into methæmoglobin, hæmoglobin is formed as an intermediate product; this undergoes a molecular rearrangement owing to the toxic action of the reacting substance, and is then oxidised to methæmoglobin. M. A. W.

Oxyhæmoglobin Fluorides. Antony Vila and M. Piettre (*Bull. Soc. chim.*, 1906, [iii], **35**, 685—688. Compare Abstr., 1905, i, 847).—The first portion of the paper is polemical against Ville and Derrien (Abstr., 1905, i, 399, 500, 622), and affirms the views put forward in the authors' previous papers (Abstr., 1905, i, 399, 500, 622, 847; ii, 402). In the second portion it is shown that the shifting of the new absorption band of oxyhaemoglobin from λ612 to λ634, brought about by the addition of minute quantities of fluorides, may be used for the detection of the latter (compare Ville and Derrien, this vol., ii, 390). The optical effect is even shown when oxyhaemoglobin is added to water in which such insoluble fluorides as those of calcium, barium, or strontium have been suspended. The simultaneous presence of phosphates, however, diminishes the sensibility of this test in the case of soluble fluorides, and may completely mask it in the case of the slightly soluble fluorides. Thus fluorine cannot be detected in bone ash, teeth ash, or apatite by this method. T. A. H.

Oxidation of Nucleic Acids. I. HANS STEUDEL (*Zeit. physiol. Chem.*, 1906, **48**, 425—429).—When copper nucleate is mixed with concentrated nitric acid, a vigorous action ensues; a similar reaction, but less violent, occurs when the nitric acid is previously diluted with its own volume of water. After several days a considerable precipitate of guanine and adenine nitrates is formed. Other products of oxidation are xanthine, hypoxanthine, thymine, uracil, and oxalic acid, products which, with the exception of oxalic acid, are also formed by the hydrolytic decomposition of nucleic acid. Pure adenine gives neither Millon's reaction nor the red coloration with diazobenzene salts in alkaline solution. J. J. S.

Lecithin-sugar and Jecorin and the Physico-chemical Behaviour of Sugar in the Blood. PAUL MAYER (*Chem. Centr.*, 1906, ii, 536—537; from *Biochem. Zeit.*, 1906, **1**, 81—107).—Lecithin-dextrose is probably a solid solution or a molecular combination of the two substances. Aqueous solutions of the substance are precipitated by sodium chloride, barium chloride, or silver nitrate. Lecithin-dextrose readily reduces an alkaline solution of copper, is fermentable, and forms an *osazone* which melts at 205°. Jecorin and lecithin-dextrose are not identical, because the sugar is firmly attached in the former compound and only loosely in the latter. The existence of a ferment in the blood which is able to split off sugar from jecorin is denied; it is, moreover, improbable that sugar occurs in the blood combined in the form of jecorin. A physiological salt solution of jecorin activates cobra poison in just the same way as lecithin. P. H.

The Rendering Insoluble of Gelatin by Oxidation Products of Phenols. AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and ALPHONSE SEYEWETZ (*Bull. Soc. chim.*, 1906, [iii], **35**, 600—602).—In addition to the developers already studied (this vol., i, 614) it is found that the phenols, gallic acid, gallotannic acid, α-naphthol, β-naphthol, resorcinol, phloroglucinol and dihydroxynaphthalene possess the property of rendering gelatin insoluble in presence of air and sodium carbonate. The rapidity with which these substances render gelatin insoluble is proportional to the readiness with which they oxidise on exposure to air in alkaline solution. T. A. H.

Action of Alums and Aluminium Salts on Gelatin. AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and ALPHONSE SEYEWETZ (*Bull. Soc. chim.*, 1906, [iii], **35**, 676—681).—Freshly-precipitated alumina and the various salts of aluminium possess the property of raising the "setting" temperature of gelatin solutions. This effect is due to the alumina, since different quantities of the various salts produce the same rise in the "setting" temperature so long as they yield the same quantity of alumina. The "setting" temperature increases proportionately with the quantity of aluminum salt until the equivalent of 0·64 gram of alumina per 100 grams of gelatin has been added. Further additions have at first no effect on the "setting" temperature, but finally cause it to fall. Gelatin is able to fix alumina, and when the latter is applied in the form of a salt, subsequent washing with water appears to dissociate the salt and remove the acid, leaving what is apparently a compound of gelatin and alumina in which the maximum possible amount of the latter present is 3·6 per cent. by weight.

T. A. H.

Peptones from Casein. ZDENKO H. SKRAUP and R. WITT (*Monatsh.*, 1906, **27**, 663—684. Compare Skraup and Zwerger, this vol., i, 123; Kossel, Abstr., 1902, i, 128; Siegfried, Abstr., 1903, i, 586; 1904, i, 953; 1905, i, 104).—The authors have repeated the investigation of Siegfried's caseinokyrine, the isolation of the kyrine being carried out under the conditions described by Siegfried. The results obtained are similar to those of Skraup and Zwerger (*loc. cit.*). The phosphotungstate of the supposed kyrine, on being fractionally extracted with 80 per cent. alcohol, yields a series of salts of different solubilities, most of which are thrown down on addition of water; the alcoholic filtrates react with picric acid, forming lysine picrate. Siegfried's caseinokyrine sulphate is free lysine.

When dissolved in dilute acetic acid and hydrolysed with 12 per cent. hydrochloric acid, casein yields a lævorotatory solution which becomes less active, but not dextrorotatory, and contains two peptones. Of these, one is precipitated by potassium mercuric iodide, contains relatively much tyrosine, histidine 0·9, arginine 1·4, and lysine 2·2 per cent. The second is precipitated by picric acid, but not by potassium mercuric iodide, contains relatively little tyrosine, histidine 2·0, and lysine 3·0 per cent., but no arginine. Both peptones give a red biuret reaction, and are precipitated from their solutions in dilute sulphuric acid on addition of a saturated solution of ammonium sulphate.

G. Y.

Decomposition of Proteid. MAX DENNSTEDT and F. HASSLER (*Zeit. physiol. Chem.*, 1906, **48**, 489—504).—An unfinished piece of work on the primary hydrolytic products (proteoses and peptones) prepared from zein, the alcohol-soluble proteid of maize. The authors' view is that the formation of such substances is not due to simple hydrolysis, but that there is also oxidation leading to the splitting off of some of the nitrogen as ammonia, and some of the sulphur as hydrogen sulphide.

W. D. H.

Influence of Light on Ferments (Invertase) in the Absence of Oxygen A. JODLBAUER and HERMANN VON TAPPEINER (*Chem. Centr.*, 1906, ii, 693; from *Münch. med. Woch.*, **53**. 653).—The influence of sunlight on the action of invertase has been examined by operating in quartz vessels which transmit ultra-violet rays. The action is measurably retarded in an atmosphere of hydrogen, nitrogen, or carbon dioxide. The retarding influence of light is not increased in an atmosphere free from oxygen when fluorescent substances are added to the solution. This result is quite different from that obtained in the presence of oxygen; in this case, fluorescent substances increase the effect of illumination many times. H. M. D.

Diastase. I. Preparation and Properties. SIGMUND FRÄNKEL and MAX HAMBURG (*Beitr. chem. Physiol. Path.*, 1906, **8**, 389—398).—The diastatic power of the malt extract is determined, and then a clear solution of basic lead acetate is added so long as the diastatic power shows no appreciable diminution. After filtration, the clear liquid should not yield a precipitate with ammonium sulphide. The liquid is passed through a Pukal filter into sterilised flasks, and is inoculated with a pure culture of Frohberg yeast, which has been previously grown in a medium rich in diastase and poor in sugar. After fermentation is completed, the liquid is drawn again through a Pukal filter into a sterilised vacuum apparatus, and is distilled under a pressure of 10 mm. until the volume is some 500 c.c. It is then fermented by a mixture of Frohberg and Logos yeasts, again filtered, and evaporated under reduced pressure, when a syrup is obtained. When dried over sulphuric acid, this forms a powder which is free from reducing or fermentable sugars and also from albumins.

The precipitation of calcium phosphate or barium sulphate in a solution of pure diastase carries down only a minute portion of the enzyme; shaking with aluminium hydroxide has the same effect. The enzyme may be completely removed from solution by the addition of colloidal ferric hydroxide, but its activity appears to be destroyed at the same time.

During electrolysis, diastase does not collect around the anode or cathode; it is, however, a colloid, as has been proved by means of the ultramicroscope. The diastase appears to be a mixture of various enzymes, and when dialysed into spring water it is largely separated into sugar forming enzymes which pass into the water and liquefying enzymes which remain within the dialysing membrane. Many organic solvents, such as alcohol or acetone, rapidly destroy the activity of pure diastase. J. J. S.

Reversible Enzyme Action. Formation and Decomposition of Esters by Pancreatic Enzymes. HENRI POTTEVIN (*Bull. Soc. chim.*, 1906, [iii], **35**, 693—696).—Most of the facts recorded have been given already in Abstr., 1903, ii, 439, 494; 1904, i, 284. It is now shown that under suitable conditions of temperature and concentration oleates of propyl, *iso*propyl, *n*-butyl, *iso*butyl, *sec.*-butyl, and *tert.*-butyl are produced by the action of the pancreatic ferment on mixtures of the appropriate alcohols with oleic acid. T. A. H.

Action of Emulsin on β-Glucosides. HUGH RYAN and GEORGE EBRILL (*Proc. Roy. Irish Acad.*, 1906, **26**, *B*, 53—55. Compare Abstr., 1904, i, 223).—The authors have tested the action of emulsin on β-*o*-tolyl arabinoside, β-carvacryl arabinoside, ββ-naphthyl arabinoside, and β-phenyl glucoside. The last compound was almost completely converted into phenol and dextrose, but in the case of the arabinosides, although faint odours of carvacrol and cresol were observed, there was no indication of even a trace of arabinose.

A table is given showing those synthetical glucosides which are hydrolysed and those which are not hydrolysed by emulsin. It is seen that the activity of emulsin towards a glucoside depends not only on the configuration of the molecule, as Fischer pointed out, but also on the nature of the groups. Thus the replacement of four hydrogen atoms in ββ-naphthyl glucoside by four acetyl groups converts a glucoside hydrolysable by emulsin into one which cannot be so hydrolysed; the conversion of salicin into its benzoyl derivative, populin, has a similar effect. T. H. P.

Action of Lipase. ALONZO E. TAYLOR (*J. Biol. Chem.*, 1906, **2**, 87—104. Compare Kastle and Loevenhart, Abstr., 1901, i, 178; Kastle, Johnston, and Elove, *ibid.*, 1904, i, 702).—All the experiments have been made with the powder obtained by repeatedly extracting castor beans with dry ether and crushing. This powder contains lipase, amylase, invertase, maltase, and an endotrypsin, but not any peroxydase. It is possible to separate lipase from the other enzymes, but the product is then much less stable. With water it forms a cloudy emulsion, and when repeatedly filtered loses its activity. When dry it may be heated above 100° without injury. Its activity is not destroyed by free acid, but when heated with water the enzyme is hydrolysed. Its action on triacetin has been studied; it has a markedly accelerating effect on the hydrolysis. The reverse process, conversion of glycerol and acetic acid into triacetin, has a very low velocity and for all practical purposes may be neglected, although in the hydrolysis a state of equilibrium is established. This equilibrium mixture has practically the same composition as the mixture formed when acids are used in the hydrolysis.

The results obtained for the hydrolysis agree with those for a unimolecular reaction and the ratio $Vt_n+10°/Vt_n=2·6$ between 18° and 28°.

In the case of triolein, Henri and Nicloux's results (*Compt. rend. Soc. Biol.*, 1904, **67**, 175) have been confirmed, namely, that t/x is constant. In this reaction the temperature coefficient is small, as an increase of 10° produces an increase of only some 20 per cent. in the velocity. The velocity measured in this case of a two-phase system is thought to be the diffusion velocity, and not the velocity of the chemical reaction. J. J. S.

Fission of Lipoid Substances by Lipase and the Optical Antipodes of Natural Lecithin. PAUL MAYER (*Chem. Centr.*, 1906, ii, 493—494; from *Biochem. Zeit.*, 1906, 1, 39—52).—Lecithin, jecorin, and protagon are readily split up by lipase; the reaction takes place in neutral solution, but less readily than in faintly acid solution. Gastric juice has no action on these substances. Ordinary dextrorotatory lecithin, when heated in a sealed tube with ten times the quantity of methyl alcohol for five or six hours at 90—100°, yields inactive lecithin in a form which is partly crystalline and partly pasty; this substance is soluble in alcohol, ether, light petroleum, or chloroform, and is only slightly soluble in acetone; when freshly prepared it is light yellow, but it soon darkens. l-*Lecithin*, which is obtained by the action of steapsin on inactive lecithin, has $[\alpha]_D - 8\cdot59°$. d-*Glycerophosphoric acid*, which is formed at the same time by the action of the lipase on the *d*-lecithin in the inactive mixture, forms white flakes and has $[\alpha]_D - 1\cdot04°$. P. H.

Nature and Effects of Rennet Coagulation. III. KARL SPIRO (*Beitr. chem. Physiol. Path.*, 1906, **8**, 365—369. Compare this vol., i, 127).—In the precipitation of cheese, free hydrogen ions are produced as in the precipitation of paracasein. The formation of cheese depends on both temperature and amount of calcium ion.

Pure casein is decomposed by rennin in a very short time, yielding albumoses. This proteolysis is not due to pepsin mixed with the rennin. J. J. S.

Specific Action of Peroxydases as Enzymes. ALEXIS BACH (*Ber.*, 1906, **39**, 3329—3331. Compare this vol., i, 616).—A reply to Chodat's claim for priority (this vol., i, 779). The so-called Chodat-Bach theory was suggested simultaneously by Engler and Bach. G. Y.

Lactic Acid Fermentation. EDUARD BUCHNER and JAKOB MEISENHEIMER (*Annalen*, 1906, **349**, 125—139).—The amount of zinc lactate obtained, and not that of the carbon dioxide liberated from calcium carbonate, must be taken as the measure of the lactic acid formed by fermentation; 2·1 and 1·25 grams respectively of zinc lactate have been obtained by the action of 10 grams each of two further enzyme preparations from *Bacillus Delbrücki* (compare Abstr., 1903, ii, 318). The enzymes become ineffective if during the preparation the heating is carried out at 90—92° for one hour. In all experiments the bacteria were killed by treatment with toluene, the resulting preparations causing neither growth nor acidification in contact with sterilised tubers at 45° for eight weeks.

It may be now considered certain that the lactic acid fermentation of sugar is caused by the action of an enzyme, the lactic acid bacteriozymase, which is a product of the living lactic acid bacteria and can be separated from it; the lactic acid is decomposed in the second stage to carbon dioxide and alcohol by the lactacidase.

A series of experiments were made with the expressed juices of *Bacillus Delbrücki*; these were not capable of forming lactic acid from sugar, the fermentative agent remaining in the residue from the expression.

As the enzyme preparation from *Bacillus Delbrücki* ferments maltose as well as sucrose, the presence of a hydrolytic enzyme must be assumed. In both cases inactive lactic acid is formed.

A 10 per cent. solution of sucrose, when treated with the enzyme preparation at 35° for one hour, has a faint reducing action towards Fehling's solution.

As both *d*- and *l*-lactic acid have been obtained by treating maltose with the living bacillus, and *d*-lactic acid has been formed in the same manner from sucrose, it is evident that the nature of the product depends on some condition such as the length of time of the fermentation, the presence of calcium carbonate, or the nature of the culture medium. G. Y.

Acetic Acid Fermentation. EDUARD BUCHNER and RUFUS GAUNT (*Annalen*, 1906, **349**, 140—184. Compare preceding abstract; Buchner and Meisenheimer, Abstr., 1903, ii, 318).—The paper opens with an account of the work of previous authors on the acetic acid fermentation of alcohol.

The activity of nine separate enzyme preparations from beer-vinegar bacteria prepared by Buchner and Meisenheimer's method was tested. The comparative activity depends on the uniformity of the acetone treatment, the genesis of the culture, and the temperature at which the pure culture is grown on the tubers; 100 grams of the most active preparation, obtained from about 220 grams of the living bacteria containing 55 per cent. of water, produced 4 grams of acetic acid. Finely powdering the enzyme does not alter the oxidising effect. Active preparations, obtained when the centrifugalised, living bacteria were dried on a porous plate before being added to the acetone, were not sterile; sterility is produced only by adding the still moist bacteria to the acetone and treating the enzyme with toluene.

In two experiments, propyl alcohol was oxidised to propionic acid by the enzyme preparation from beer-vinegar bacteria. It may be regarded as certain that the acetic acid fermentation of alcohol is caused by an enzyme, to be called the alcohol-oxydase, which is a product of the vinegar bacillus. The ash of the bacteria contains an amount of iron equivalent to 0·08 per cent. of the enzyme preparation, which in alcoholic guaiacum resin solution gives a transient coloration with hydrogen peroxide.

The relation of the alcohol-oxydase to other known oxidising enzymes is discussed.

The expressed juice of the beer-vinegar bacteria does not oxidise alcohol in the presence of air (compare preceding abstract).

The results of the experiments described are given in a series of tables. G. Y.

Organic Chemistry.

Alkaline Aqueous Mercuri-iodide as a Reagent for Hydroxyl Groups. Leopold Rosenthaler (*Arch. Pharm.*, 1906, **244**, 373—375).—When boiled for one minute with Nessler's solution, substances which contain a primary or a secondary alcohol group bring about a reduction of the solution (to metallic mercury). Substances containing a tertiary alcoholic group do not effect this reduction. The action of substances containing phenolic groups is varied.

Sachsse's (alkaline mercuri-iodide) solution reacts in the same way, but not Knapp's (alkaline mercuricyanide) solution. C. F. B.

Preparation of Chemically Pure Methyl and Ethyl Alcohols; their Specific Gravities. Peter Klason and Evert Norlin (*Arkiv Kem. Min. Geol.*, 1906, **2**, No. 24, 1—7).—Chemically pure methyl or ethyl alcohol may be prepared as follows: 500 grams of pure potassium methyl (or ethyl) sulphate are dissolved in water, and to the solution rather more than the calculated quantity of pure sulphuric acid is added, the whole liquid measuring about 2 litres. The methyl (or ethyl) alcohol is distilled in a current of steam and concentrated by fractionation, finally, from ignited potassium hydroxide. To remove the last traces of moisture, freshly ignited lime (from marble) and, finally, calcium are used. Distillation from calcium is continued until the specific gravity of the alcohol undergoes no further change.

Pure methyl alcohol has the sp. gr. 0·796472 at 15°/15°, and, between 0° and 30°, the sp. gr. at $t°/4°$ is expressed by $0·80999 - 0·00093\,t - 0·00000025\,t^2$.

Pure ethyl alcohol has the sp. gr. 0·794130 at 15°/15°; the value 0·79429, on which Windisch's tables are calculated, indicates that the alcohol used by this author contained 0·05 per cent. of water. Its sp. gr. at 0°/4° is 0·80628; at 10°/4°, 0·79792; at 20°/4°, 0·78938; at 30°/4°, 0·78080. These values agree well with those obtained by Winkler. T. H. P.

sec.- **and** *tert.*-**Pinacolyl Alcohols and their Separation.** Maurice Delacre (*Bull. Soc. chim.*, 1906, [iii], **35**, 811—816. Compare this vol., i, 476, 518, 551, 784).—*tert.*-Pinacolyl alcohol was obtained by the application of the Grignard reaction to *iso*propyl bromide. Its odour is similar to that of the alcohol prepared from pinacolin, and after the removal of traces of impurity by shaking it with solid potassium hydroxide, it boils at 118·4—119·2° under 748 mm. pressure and freezes about 10·5°. The chloride boils from 112—113·4° and solidifies at 7°; the acetate, obtained by warming the alcohol with acetic anhydride for several hours, boils from 125—140°. When the alcohol is heated with the anhydride in a closed tube for three days at 200°, the principal product is tetramethylethylene

($\beta\gamma$-dimethyl-Δ^{β}-butylene). The *tert.*-pinacolyl alcohol (and also the alcohol regenerated from the acetate described above) is dehydrated by dilute sulphuric acid much more rapidly than the alcohol obtained from pinacolin, and this method may be used for their separation.

The synthetic *tert.*-pinacolyl alcohol and the alcohol obtained from pinacolin appear therefore to be distinct substances possessing different physical properties, but yielding the same derivatives (chloride, bromide, acetate). The formation of the same derivatives from the two alcohols is similar to the transformation of the group

$$CMe_3{\cdot}CH{:}CH_2$$

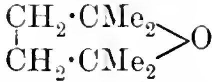
into $CMe_2{:}CMe_2$ by the action of hydrogen bromide on $\gamma\gamma$-dimethyl-Δ^{a}-butylene (this vol., i, 477). T. A. H.

Succinic Pinacone [$\beta\epsilon$-Dimethylhexane-$\beta\epsilon$-diol],

$$OH{\cdot}CMe_2{\cdot}CH_2{\cdot}CH_2{\cdot}CMe_2{\cdot}OH.$$

Louis Henry (*Compt. rend.*, 1906, **143**, 496—500).—$\beta\epsilon$-Dimethylhexane-$\beta\epsilon$-diol (compare Zelinsky, Abstr., 1902, i, 593; and Valeur, *Bull. Soc. chim.*, 1902, **27**, 1139), readily obtained by the action of magnesium methyl bromide on ethyl lævulate, behaves like a tertiary alcohol (this vol., i, 133, 329), and reacts with fuming hydrochloric acid or acetyl chloride to form $\beta\epsilon$-dichloro-$\beta\epsilon$-dimethylhexane,

$$CMe_2Cl{\cdot}CH_2{\cdot}CH_2{\cdot}CMe_2Cl,$$

which crystallises in plates or needles melting at 66—67°, boils and decomposes at 180°, and is identical with the compound obtained by the action of hydrochloric acid on di*iso*crotonyl or di*iso*butenyl (Pogorželsky, Abstr., 1899, i, 785). $\beta\epsilon$-Dimethylhexane-$\beta\epsilon$-diol is readily dehydrated by the action of dilute sulphuric acid even in the cold to form *s*-tetramethyltetramethylene oxide,  $\begin{matrix} CH_2{\cdot}CMe_2 \\ | \\ CH_2{\cdot}CMe_2 \end{matrix}\!\!>\!O$ (compare Pogorželsky, Abstr., 1899, i, 785), which is a colourless, mobile liquid with an agreeable odour, boils at 116—117°, and reacts even in the cold with fuming hydrochloric acid to form $\beta\epsilon$-dichloro-$\beta\epsilon$-dimethylhexane. When $\beta\epsilon$-dimethylhexane-$\beta\epsilon$-diol is distilled, it suffers partial dehydration and forms the unsaturated *alcohol*

$$CMe_2{:}CH{\cdot}CH_2{\cdot}CMe_2{\cdot}OH$$

[*$\beta\epsilon$-dimethyl-Δ^{ϵ}-hexylene-β-ol*], which is a colourless, mobile liquid with an agreeable penetrating odour, boils at 165°, combines readily with bromine, and is converted into its *chloride* by the action of acetyl chloride. M. A. W.

Distillation of Ether. E. J. Swaab (*Chem. Centr.*, 1906, ii, 841; from *Pharm. Weekblad*, 1906, **43**, 817—818).—A glass attachment is described, enabling a reflux condenser to be used, the condensed ether passing down a vertical tube into the receiver, the vapour entering by means of a side branch. P. H.

Freezing and Melting Points of Glyceryl Nitrate. Hermann Kast (*Chem. Centr.*, 1906, ii, 948; from *Zeit. ges. Schiess, Sprengstoffwesen*, **1**, 225—228).—Glyceryl nitrate exists in two modifications. The labile form melts at 2·8—2·9° and solidifies at 2·0—2·2°, whilst the stable form melts at 13·1—13·2° and solidifies at 12·5°. The labile form has a more glassy appearance than the other. It is very difficult to freeze small quantities, but less so to freeze large quantities, of glyceryl nitrate; in a mixture of ether and carbon dioxide it solidifies to an amorphous mass which, however, becomes liquid on warming to temperatures below the true freezing point; when once it has been frozen it is less difficult to freeze it a second time. The depression of the freezing point of glyceryl nitrate by dinitrochlorohydrin agrees fairly closely with Raoult's law. P. H.

Origin of Optically Active Fatty Acids in Nature. Carl Neuberg (*Chem. Centr.*, 1906, ii, 1132—1133; from *Biochem. Zeit.*, 1906, 1, 368—379).—The author has obtained experimental evidence in support of his theory that mineral oil originates from the optically active decomposition products of proteids. The fatty acids isolated from a sample of putrid cheese yielded a fraction comprising from acetic to hexoic acid which had α_D + 1·2°. The volatile acids obtained from putrid gelatin were similarly active, but to a less degree. Further, by the action of lipase from vegetable sources on the triglyceride of dibromostearic acid, free dextrorotatory dibromostearic acid and a dextrorotatory glyceride were obtained, showing that as a result of slow oxidation and asymmetric fission by living or unorganised ferments, inactive fats may give rise to optically active substances.

P. H.

Active Components of α-Bromopropionic Acid. Ludwig Ramberg (*Annalen*, 1906, **349**, 324—332. Compare Abstr., 1901, i, 63; Warburg and Fischer, Abstr., 1905, i, 692).—The resolution of the inactive acid can be effected without great loss of material by a method involving fractional crystallisation of the cinchonine salt and "freezing" out the inactive acid from the active acids so obtained. A supersaturated solution of the salt, $C_{19}H_{22}ON_2,2C_3H_5O_2Br$, is made by dissolving 153 grams of the acid and 148 grams of cinchonine in 3 litres of water at 30—35°, the last 25 per cent. of the acid being added slowly after the base has dissolved. After evaporating the solution at 27—30° in a vacuum to 2,300 c.c., the crystals (fraction I.) are removed and the mother liquor evaporated to about 1,400 c.c. and the second crop of crystals (fraction II.) filtered off. The solution of these crystals is employed in dissolving a fresh quantity of cinchonine and of the racemic acid. The acid from fraction I. (α_D − 11°) and that from the mother liquor from fraction II. (α_D + 19°) are treated separately as follows. The temperature is raised to the highest at which crystallisation will begin, the acid is nucleated with a crystal of the racemic form, and the temperature allowed to fall very slowly for several days. When half the acid has solidified, the crystals are separated centrifugally, and consist of the pure racemic form. The liquid is again nucleated and cooled slowly to 0°, whereby a further quantity of the racemic form is obtained. The acid which still remains liquid has α_D ± 33°, and after a third nucleation at − 5°, cooling to − 15°, and removal of the crystals, has α_D ± 38°. The cinchonine salt of this acid is recrystallised six or eight times from water or acetone. The recovered *l*-α-bromopropionic acid solidifies completely at − 40°;

when the temperature is raised slowly to $-7°$ and then lowered to $-12°$, the crystals obtained, after removal of the liquid portion, consist of the pure lævo-acid. It melts at $-6°$ to $-7°$, has a sp. gr. 1·708 at 20°/20°, and $[\alpha]_D$ $-27°$ at 20° (compare Warburg, *loc. cit.*). The pure *d*-acid has not been obtained; the *ethyl* ester of an acid having α_D $+36·33°$ boils at 62—63° under 15 mm. pressure, has a sp. gr. 1·388 at 20°/4°, and α_D $+36·35°$ at 20°. The pure ester should have α_D $+46°$ and $[\alpha]_D$ $+33°$ at 20° (compare Walker, Trans., 1895, **67**, 921). C. S.

Theory of Saponification. JULIUS MARCUSSON (*Ber.*, 1906, **39**, 3466—3474).—According to Lewkowitsch (Proc., 1899, **15**, 190) incompletely hydrolysed fats should contain mono- and di-glycerides, and the presence of these substances should be indicated by a high acetyl value; but as other compounds, such as hydroxy-acids, lactones, &c., are also indicated by the acetyl value, the author has endeavoured to isolate the lower glycerides and thus obtain further support for the theory of successive hydrolysis.

A quantity of incompletely saponified fat was divided into two equal parts. One was acidified, and the precipitated neutral fat and free fatty acid acetylated directly; from the other portion, after removing excess of alkali with acid, the soaps were extracted and the residual neutral fat acetylated. Finally, the fatty acids from the soaps of the second portion were acetylated. The anticipated increase in the acetyl value was never observed. The portion containing both neutral fat and free fatty acid usually gave a slightly higher acetyl value than that of the neutral fat, and the acetyl value of the separated acids were sometimes as high as, and sometimes higher than, that of the neutral fat. These results do not point to the existence of the lower glycerides, but seem to depend on certain changes which have occurred in the fatty acids.

The saponification of olive oil by shaking with concentrated aqueous sodium hydroxide in stoppered vessels excludes the interference of atmospheric oxygen and affords scope for the hydrolysis to occur in successive stages, but no indication of the formation of the lower glycerides was obtained. Saponification of this oil in the cold with the enzyme of castor oil seeds gave no indication of successive hydrolysis. The hydrolytic changes which occur in rancid fats do not give rise to the lower glycerides, for although dierucein is found in old rape-seed oil, yet it only occurs in the oil which has been refined with sulphuric acid, and in all probability arises as a fission product of trierucein, formed, not by alkaline hydrolysis, but by the action of the acid. The examination of rancid sheep's tallow and olive oil gave no indubitable evidence of the presence of mono- and di-glycerides.

G. T. M.

Beeswax from Annam. J. BELLIER (*Ann. Chim. anal.*, 1906, **11**, 366—368).—A sample of yellow beeswax received from Annam gave results, on analysis, which differed considerably from those yielded by ordinary European beeswax. The figures obtained were: sp. gr. 0·964; m. p. 61°; acid number, 7·8; ester number, 86·6; iodine number, 6; unsaponifiable matter, 10·5 per cent. W. P. S.

Historical Note on the Fixation of Ozone by Oleic Acid. THEODOR WEYL (*Ber.*, 1906, **39**, 3317—3318).—The author claims to have been the first to observe the fixation of ozone by acids of the oleic series (compare Molinari, this vol., i, 792; Harries, *ibid.*, i, 793).

E. F. A.

Separation of the Fatty Acids of Cod-liver Oil. HENDRIK BULL (*Ber.*, 1906, **39**, 3570—3576. Compare Abstr., 1900, ii, 250, 325; 1901, ii, 137; Ljubarsky, Abstr., 1898, ii, 299).—The fatty acids of cod-liver oil are separated by conversion into the methyl esters, fractional distillation of these under 10 mm. pressure, when 80 per cent. of the esters distil below 240°, and hydrolysis of the fractions so obtained. In this manner have been isolated myristic, palmitic, stearic, oleic, and erucic acids, as also two new acids, $C_{16}H_{30}O_2$, and $C_{20}H_{38}O_2$.

The unsaturated *acid* $C_{16}H_{30}O_2$, which is present to the extent of 6 per cent. of the cod-liver oil, and is obtained also from herring and whale oils, melts at −1°, has an acid number 219, and an iodine number 91·5, forms a *methyl* ester boiling at 185—186° under 10 mm. pressure, and on oxidation with potassium permanganate in alkaline solution cooled with ice, yields a *dihydroxypalmitic acid* crystallising in white leaflets and melting at 125°. The *acetyl* derivative of this acid has an acetyl number 355·7.

Gadoleic acid, $C_{20}H_{38}O_2$, obtained together with stearic and oleic acids on hydrolysis of the fraction boiling at 205—206° under 10 mm. pressure, occurs also in herring and whale oils; it melts at 24·5°, and has an acid number 180·5, and an iodine number 80·3. On oxidation with potassium permanganate in alkaline solution cooled with ice, it yields *dihydroxygadic acid*, $C_{20}H_{38}O_2(OH)_2$, which separates from alcohol in white crystals, melts at 127·5—128°, and has an acid number 161·7.

Heyerdahl's jecoleic acid (*Cod-liver Oil and its Chemistry*), if present, can be so only in very small amount, whilst this author's dihydroxy-acid is probably a eutectic compound of oleic and gadoleic acids.

G. Y.

Action of Alkali Carbonates on βγ-Dibromo-αα-dimethyl Acids. Part II. ALFRED COURTOT (*Bull. Soc. chim.*, 1906, [iii], **35**, 969—988. Compare this vol., i, 788).—βγ-Dibromo-ααβ-trimethylbutyric acid, on treatment with zinc dust, furnishes dimethyl*iso*propenylacetic [αα-dimethyl-β-methylenebutyric] acid, and reacts with a dilute solution of potassium hydrogen carbonate, forming dimethyl*iso*propenylcarbinol. With potassium carbonate the action proceeds further, and in addition to the alcohol some pinacolin and di*iso*propenyl are formed. The latter is the principal product obtained when βγ-dibromo-ααβ-trimethylbutyric acid is treated with pyridine in presence of ether.

Dimethyl*iso*propenylcarbinol, $CH_2\colon CMe\cdot CMe_2\cdot OH$, is a mobile liquid of pleasant odour, melts at −17° (compare Choupotsky and Mariutza, Abstr., 1890, 727). The *phenylcarbamate* separates from boiling light petroleum in long needles and melts at 103—104°. On dehydration with sulphuric acid, the alcohol yields a mixture of di*iso*propenyl and pinacolin. Di*iso*propenyl [$\beta\gamma$-dimethyl-$\Delta^{\alpha\gamma}$-butadiene],

$$CH_2{:}CMe{\cdot}CMe{:}CH_2,$$

has a sp. gr. 0·73074 at 15°, n_α 1·4379, n_β 1·4527, n_γ 1·4622, and n_D 1·4421, and on oxidation with permanganate yields acetic and formic acids and a small quantity of pinacolin. The dibromide, $CH_2Br{\cdot}CMeBr{\cdot}CMe{:}CH_2$, melts at 49°, boils at 105° under 14 mm. pressure, and regenerates the hydrocarbon on treatment with magnesium in presence of ether (compare Kondakoff, Abstr., 1901, i, 62). The tetrabromide melts at 140° [compare (1) Mariutza and (2) Kondakoff (*loc. cit.*)]. The oily bromide referred to by Kondakoff (*loc. cit.*) boils at 115° under 14 mm. pressure, and is probably a mixture of the dibromide with other more highly brominated derivatives.

Dimethylallylcarbinol, $CH_2{:}CH{\cdot}CH_2{\cdot}CMe_2{\cdot}OH$, obtained by condensing acetone with allyl iodide in presence of zinc, is a mobile liquid and boils at 120° under atmospheric pressure (compare Saytzeff, Abstr., 1877, ii, 298). The *phenylcarbamate* crystallises from boiling light petroleum in slender needles and melts at 49—50°.

When ethyl methylacrylate reacts with magnesium methyl iodide, dimethyl*iso*propenylcarbinol, di*iso*propenyl, and *$\alpha\alpha$-methylethylacetone* [*methyl α-methylpropyl ketone*] are produced (compare Kohler, Abstr., 1904, i, 595). $\alpha\alpha$-Methylethylacetone may also be prepared by treating ethyl acetoacetate with ethyl and methyl iodides successively in presence of sodium and alcohol and hydrolysing the complex ester so formed. The ketone is liquid, has a penetrating camphoraceous odour, and boils at 116° under atmospheric pressure; the *semicarbazone* crystallises from ether and melts at 95—96°; the *oxime* is a pungent smelling liquid and boils at 89° under 20 mm. pressure; the *phenylhydrazone* is viscid and boils at 152° under 10 mm. pressure.

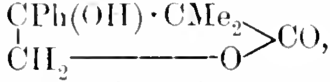
*Diethyl*iso*propenylcarbinol*, $CH_2{:}CMe{\cdot}CEt_2{\cdot}OH$, the sole product of the action of magnesium ethyl iodide on ethyl methylacrylate, is a mobile liquid with a camphoraceous odour and boils at 152°.

Methylpropenylcarbinol, $CHMe{:}CHMe{\cdot}CH{\cdot}OH$, the sole product of the action of magnesium methyl iodide on crotonaldehyde, boils at 122° under atmospheric pressure (compare Grignard, Abstr., 1901, i, 679); the *acetate* boils at 138°, and the *phenylcarbamate* crystallises from light petroleum and melts at 43°.

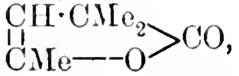
By the action of magnesium methyl iodide on ethyl $\beta\beta$-dimethylacrylate, dimethylpentadiene, dimethyl*iso*butenylcarbinol, and a *ketone* yielding a *semicarbazone* crystallising in long needles and melting at 123—124° are obtained. This ketone may be ψ-butylacetone, $CMe_3{\cdot}CH_2{\cdot}COMe$. Attempts to synthesise ψ-butylacetone by condensing *tert.*-butyl chloride with trioxymethylene in presence of magnesium yielded only Tissier's alcohol, $CMe_3{\cdot}CH_2{\cdot}OH$. The *iodide* prepared from the latter, by condensation with acetyl chloride in presence of zinc, yielded only traces of the ketone sought, and similarly attempts to prepare the ketone from ethylacetoacetate were unsuccessful.

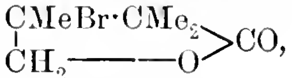
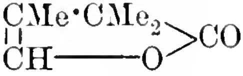
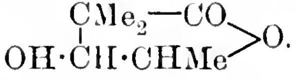
Dimethyl*iso*butenylcarbinol, $CMe_2{:}CH{\cdot}CMe_2{\cdot}OH$, is the principal product of the interaction of magnesium methyl iodide and ethyl methylacrylate. It has a camphoraceous odour and boils at 138° under atmospheric pressure (compare von Fellenberg, Abstr., 1904, i, 961). The *phenylcarbamate* crystallises in silky needles and melts at 111°. βδ-Dimethyl-Δ^{αγ}-pentadiene, $CMe_2\colon CH\cdot CMe\colon CH_2$, also produced in the above reaction (compare Grignard, Abstr., 1900, i, 382), boils at 90° under atmospheric pressure; the *dibromide* has an irritating odour and boils at 65° under 10 mm. pressure.

The foregoing results show that the fixation of magnesium alkyl haloids by the αβ-unsaturated esters of the aliphatic series is confined to magnesium methyl iodide, and in this respect differ from those obtained by Kohler (Abstr., 1904, i, 595) and by Kohler and Heritage (Abstr., 1905, i, 207) with unsaturated compounds of the cyclic series.

When βγ-dibromo-β-phenyl-αα-dimethylbutyric acid is treated with an aqueous solution of potassium carbonate, *β-hydroxy-β-phenyl-αα-dimethylbutyrolactone,*  $\begin{array}{l}CPh(OH)\cdot CMe_2\\ |\\ CH_2\text{———————}O\end{array}\!>\!CO$, and *phenylisoprene* are produced. The former crystallises from a mixture of ether and light petroleum and melts at 115°. Phenylisoprene is a mobile odorous liquid, boils at 95° under 24 mm. pressure and yields a liquid dibromide. When dissolved in carbon disulphide and treated with bromine, it furnishes a crystalline *product* which may be a monobromo-derivative of the dibromide; it melts at 76°. T. A. H.

γ-Aldehydo-acids. EDMOND E. BLAISE and ALFRED P. COURTOT (*Bull. Soc. chim.*, 1906, [iii], **35**, 989—1004. Compare Abstr., 1905, i, 562).—When βγ-dibromo-αα-dimethylbutyric acid is distilled, it decomposes, yielding γ-bromo-αα-dimethylbutyrolactone (this vol., i, 788), and this, when boiled with quinoline, furnishes isoprene. Ethyl βγ-dibromo-αα-dimethylbutyrate, obtained by the action of bromine on ethyl dimethylvinylacetate, is readily hydrolysed either by potassium hydroxide or acetate dissolved in water, and therefore yields the same products as the free acid when treated with these reagents.

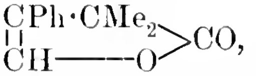
β-Bromo-αα-dimethylvalerolactone, when heated in presence of quinoline, yields the corresponding unsaturated lactone,  $\begin{array}{l}CH\cdot CMe_2\\ \|\\ CMe\text{——}O\end{array}\!>\!CO$, and this, when dissolved in an aqueous solution of potassium hydroxide, yields mesitonic acid, $CH_2Ac\cdot CMe_2\cdot CO_2H$.

βγ-Dibromo-ααβ-trimethylbutyric acid (Abstr., 1905, i, 562) crystallises from light petroleum and melts at 107—108°. When heated, it furnishes first the corresponding bromolactone,  $\begin{array}{l}CMeBr\cdot CMe_2\\ |\\ CH_2\text{————}O\end{array}\!>\!CO$, which crystallises in parallelopipeds and melts at 194°, and finally the unsaturated lactone,  $\begin{array}{l}CMe\cdot CMe_2\\ \|\\ CH\text{————}O\end{array}\!>\!CO$, which is crystalline at low temperatures, melts at −25°, boils at 65° under 12 mm. or at 174° under atmospheric pressure, and on hydrolysis (*loc. cit.*) furnishes γ-hydroxy-ααβ-trimethylbutyrolactone,  $\begin{array}{l}\quad\ CMe_2\text{—}CO\\ \quad\ \ |\\ OH\cdot CH\cdot CHMe\end{array}\!>\!O$. The *ethyl ether* of this is a mobile liquid and boils at 107° under 11 mm. pressure; the acetate (*loc. cit.*) boils at 135° under 11 mm. pressure. On treatment with semicarbazide hydrochloride in presence of sodium acetate, the hydroxylactone yields *trimethylsuccinic hemialdehyde semicarbazone*, $NH_2{\cdot}CO{\cdot}NH{\cdot}N{:}CH{\cdot}CHMe{\cdot}CMe_2{\cdot}CO_2H$, which forms small crystals and melts and decomposes at 240°. The corresponding *oxime*, obtained in an analogous manner, melts and decomposes at 153°, and the *phenylhydrazone* melts at 110°.

On oxidation with chromic acid, γ-hydroxy-*aaβ*-trimethylbutyrolactone yields trimethylsuccinic acid.

βγ-Dibromo-aaβ-trimethylbutyrolactone, obtained by the action of bromine on the unsaturated bromolactone mentioned previously, melts at 107—108°.

*γ-Bromo-aa-dimethyl*iso*propenylacetic acid*, $CHBr{:}CMe{\cdot}CMe_2{\cdot}CO_2H$, obtained by heating methyl βγ-dibromo-*aaβ*-trimethylbutyrate with potassium hydroxide dissolved in water, crystallises from light petroleum and melts at 59°. Its *methyl ester*, prepared from βγ-dibromo-*aaβ*-trimethylbutyrate, is a mobile liquid and boils at 104° under 19 mm. pressure.

β-Bromo-β-phenyl-aa-dimethylbutyrolactone, obtained by heating βγ-dibromo-β-phenyl-*aa*-dimethylbutyric acid at 220° under 30 mm. pressure, crystallises from a mixture of ether and light petroleum in brilliant lamellæ, melts at 131°, and, when boiled with quinoline, yields *phenyldimethylbutenolide*,  $\left.\begin{array}{l}\mathrm{CPh{\cdot}CMe_2}\\ \Vert \\ \mathrm{CH{-\!-\!-\!-}O}\end{array}\right\rangle\mathrm{CO}$, which crystallises from ether, melts at 70—71°, boils at 145° under 10 mm. pressure, and on hydrolysis yields *γ-hydroxy-β-phenyl-aa-dimethylbutyrolactone*. This forms brilliant spangles from benzene, begins to decompose at 120°, melts at 131°, and, with semicarbazide hydrochloride in presence of sodium acetate, yields *phenyldimethylsuccinic hemialdehyde semicarbazone*, which crystallises from alcohol and melts and decomposes at 220°. The corresponding *oxime* is crystalline, begins to decompose at 140°, and melts at 155°. The *hydroxylamine* salt of the oxime melts and decomposes at 130°. By the action of hydrazine hydrate on the γ-hydroxy-lactone (2 mols.), *phenyldimethylsuccinic hemialdehydeazine*, $N_2({:}CH{\cdot}CHPh{\cdot}CMe_2{\cdot}CO_2H)_2$, is produced; it crystallises from alcohol and melts at 210°.

β-Phenyl-aa-dimethylsuccinic acid, obtained by oxidising the hydroxylactone with chromic acid, separates from ether in small crystals and melts and decomposes at 180°. T. A. H.

Preparation of Methylethylpyruvic Acid and its Derivatives. René Locquin (*Bull. Soc. chim.*, 1906, [iii], **35**, 962—965).—Most of the facts recorded in this paper are already given in Abstr., 1905, i, 636. Ethyl *sec.*-butylacetoacetate, prepared by the general method (Abstr., 1904, i, 646), yields with hydrazine hydrate, 3-*methyl*-4-sec.-*butyl*-5-*pyrazolone*, which crystallises from boiling benzene and melts at 158—159°. When ethyl *sec.*-butylacetoacetate is treated with nitrosylsulphuric acid (Bouveault and Locquin, Abstr., 1904, i, 847), it furnishes ethyl *a*-oximino-β-methylvalerate (Abstr., 1905, i, 636), a thick liquid which has a sp. gr. 1·042 at 0°/4°. This is hydrolysed by potassium hydroxide in water and furnishes the corresponding acid (*loc. cit.*), which separates from ether in brilliant spangles and melts, sublimes, and decomposes at 160—161°. Further, the ethyl methylethylpyruvate, formed by treating the oximino-ester with freshly-formed nitrous acid (Bouveault and Locquin, Abstr., 1905, i, 10), is a colourless liquid which has a sp. gr. 0·988, boils at 78—79° under 15 mm. pressure, and is hydrolysed less easily than its analogues. The semicarbazone separates, on cooling its solution in light petroleum, in slender needles, melts at 82—83°, and, on treatment with potassium hydroxide solution at 100°, furnishes, not the semicarbazone of methylethylpyruvic acid, but the corresponding *lactam*,

$$\mathrm{CHMeEt{\cdot}C}{<}\begin{matrix}\mathrm{CO{\cdot}NH}\\ \mathrm{N{-}NH}\end{matrix}{>}\mathrm{CO},$$

which crystallises from benzene on addition of alcohol in spangles and melts at 206—207°.

Ethyl methylethylpyruvate, when heated with water in a closed tube for several hours, furnishes the acid which boils at 84° under 15 mm. pressure (?), melts at 35°, furnishes a phenylhydrazone melting at 130° and a semicarbazone which crystallises from dilute alcohol and melts at 165°. T. A. H.

[β-Ethoxymethylacrylic Acid]. OSKAR EMMERLING and L. KRISTELLER (*Ber.*, 1906, **39**, 3549—3550).—β-Ethoxymethylacrylic acid, recently described by the authors (this vol., i, 623), is the same substance as that prepared lately by Tschitschibabin (this vol., i, 398). G. T. M.

Isomorphism. JEAN HERBETTE (*Chem. Centr.*, 1906, ii, 970; from *Bull. Soc. franç. Min.*, **29**, 97—190).—By special methods of crystallisation the following new crystalline forms of previously known compounds have been obtained. (1) A rhombohedral form of thallium tartrate, $C_4H_4O_6Tl_2$[$a:c = 1:1·08534$], sp. gr. 4·8; (2) a rhombic hydrated thallium tartrate, $2C_4H_4O_6Tl_2,H_2O$; these salts are completely isomorphous with the rubidium and potassium salts respectively; (3) a substance obtained by crystallising a mixture of barium chloride and bromide. For details of these compounds the original paper should be consulted. P. H.

Action of Formaldehyde Solution on Potassium Permanganate. GEORGE B. FRANKFORTER and RODNEY M. WEST (*J. Amer. Chem. Soc.*, 1906, **28**, 1234—1238).—A study on the action of formalin on solid potassium permanganate. In order to avoid a too violent action, the powdered permanganate should be diluted with an equal bulk of sand. In order to obtain the largest possible amount of gaseous formaldehyde (which may then be absorbed in water and titrated), 50 c.c. of strong formalin should be dropped slowly (so as to take about thirty minutes) on to 200 grams of the permanganate-sand mixture. A special apparatus is described and illustrated, and two tables are given. L. DE K.

Action of Bases on Chloral Hydrate. JOHANNES E. ENKLAAR (*Rec. trav. chim.*, 1906, **25**, 297—310).—The author has extended his investigation on the rate of decomposition of chloral hydrate by the action of bases (Abstr., 1905, i, 171, 741), and in the present paper the values of the velocity coefficient are tabulated for mixtures of chloral hydrate and barium hydroxide, with and without the addition of neutral barium nitrate, chloride, acetate, propionate, or valerate. The results show that, as in the case of the other alkali or alkali-earth hydroxides, the velocity of the reaction increases with the excess of the free base above the equivalent of the chloral hydrate employed, and is accelerated by the addition of neutral salts, equivalent quantities of different salts producing the same effect. M. A. W.

Succinaldehyde Derivatives. CARL D. HARRIES and HERMANN KRÜTZFELD (*Ber.*, 1906, **39**, 3670—3677. Compare Abstr., 1901, i, 451; 1902, i, 345; this vol., i, 227; Wohl and Schweitzer, *ibid.*, i, 232).—In the preparation of succindialdehyde from its dioxime by means of nitrous gases, it is advisable to pass the gases for some time after all the oxime has dissolved, as otherwise, after neutralising with calcium carbonate and evaporating, an explosive syrup is obtained. If the gas is passed for too long a time a precipitate of succinic acid appears.

Succinaldehydedisemicarbazone, $C_6H_{12}O_2N_6,H_2O$, crystallises from water, in which it is readily soluble, in the form of six-sided prisms, melting at 188°. It dissolves readily in methyl, less readily in ethyl alcohol. The diphenylmethylhydrazone melts at 96°, and not at 86° (Henle, Abstr., 1905, i, 413).

The *di-nitrophenylhydrazone* $C_{16}H_{16}O_4N_6,H_2O$, crystallises in golden yellow needles melting at 185° and is insoluble in water.

The product $C_{10}H_{10}N_2,H_2O$, obtained by the condensation of succinaldehyde with *o*-phenylenediamine, is a yellow, amorphous powder with feebly basic properties. It melts at about 150°, but after heating at 100° is anhydrous and then melts at about 177°. It dissolves in benzene or chloroform, but is insoluble in water, alcohol or light petroleum.

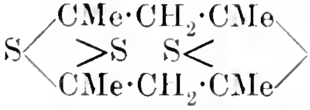
Succintetramethylacetal is readily converted into its *dibromo*-derivative, $CH(OMe)_2{\cdot}CHBr{\cdot}CHBr{\cdot}CH(OMe)_2$, when treated with an excess of bromine in the presence of calcium carbonate in sunlight. It is a colourless oil readily soluble in organic solvents, and when heated evolves hydrogen bromide.

Dibromosuccinaldehyde, obtained by brominating the aldehyde in chloroform solution in the presence of calcium carbonate, is a yellow oil with a strong odour. It readily reduces Fehling's solution, but does not give the pyrrole reaction. When dissolved in warm acetic acid and precipitated with water, it is converted into a solid modification melting at 75° after sintering at about 50°.

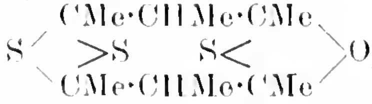
When distilled under reduced pressure, the dibromo-derivative is converted into *bromofumaraldehyde*, which distils at 130° under 15 mm. pressure. The *tetra-acetal* distils at 110—120° under 15 mm. pressure.

J. J. S.

Thio-derivatives of Ketones. III. EMIL FROMM and PAUL ZIERSCH (*Ber.*, 1906, **39**, 3599—3609. Compare Baumann and Fromm, Abstr., 1890, 26; 1895, i, 362; Fromm and Mangler, Abstr., 1901, i, 184).—1 : 3-Diketones react with hydrogen sulphide in presence of hydrogen chloride, forming thio-derivatives of the bisdiketones.

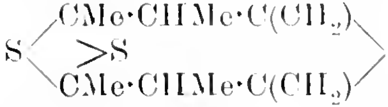
Tetrathiobisacetylacetone,  separates from boiling alcohol in white crystals, melts at 161°, remains unchanged when boiled with alcoholic potassium hydroxide, or when distilled alone or with zinc dust or copper powder, dissolves in concentrated sulphuric acid and is reprecipitated on dilution, and reacts with bromine in chloroform solution, evolving hydrogen bromide and forming an unstable crystalline *substance.* When heated with methyl iodide at 100°, it yields trimethylsulphine iodide.

With hydrogen sulphide methylacetylacetone yields two products: *trithio-oxybismethylacetylacetone,*



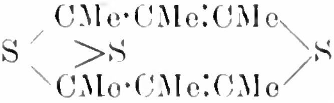
$$\mathrm{S}\left<\begin{array}{c}\mathrm{CMe{\cdot}CHMe{\cdot}CMe}\\ >\mathrm{S}\qquad\mathrm{S}<\\ \mathrm{CMe{\cdot}CHMe{\cdot}CMe}\end{array}\right>\mathrm{O}$$

which melts at 100°, is readily soluble in chloroform or alcohol, and is obtained only in a slightly impure condition, and *trithiobismethylacetylacetone,*



$$\mathrm{S}\left<\begin{array}{c}\mathrm{CMe{\cdot}CHMe{\cdot}C(CH_2)}\\ >\mathrm{S}\\ \mathrm{CMe{\cdot}CHMe{\cdot}C(CH_2)}\end{array}\right>\mathrm{S}$$

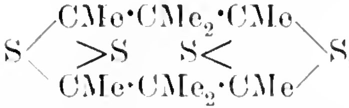
or



$$\mathrm{S}\left<\begin{array}{c}\mathrm{CMe{\cdot}CMe{:}CMe}\\ >\mathrm{S}\\ \mathrm{CMe{\cdot}CMe{:}CMe}\end{array}\right>\mathrm{S}$$

which is precipitated on addition of alcohol to its solution in chloroform and melts at 193°.

Tetrathiobisdimethylacetylacetone,



$$\mathrm{S}\left<\begin{array}{c}\mathrm{CMe{\cdot}CMe_2{\cdot}CMe}\\ >\mathrm{S}\qquad\mathrm{S}<\\ \mathrm{CMe{\cdot}CMe_2{\cdot}CMe}\end{array}\right>\mathrm{S}$$

melts at 227°, and is soluble in chloroform, but insoluble in alcohol.

These thio-derivatives of the 1 : 3-diketones are oxidised by shaking the benzene solution with concentrated aqueous potassium permanganate and dilute sulphuric acid.

Tetrathiobisacetylacetone yields two oxidation products: *trithiotetraoxybisacetylacetone,* $C_8H_{14}O_4S_3$, melts at 275°, is soluble in hot water, but is almost insoluble in cold water or alcohol, and is decomposed by aqueous alkali hydroxides. *Trithiotrioxybisacetylacetone,* $C_8H_{14}O_3S_3$, crystallises from water in which it is more soluble than the tetrathiotetraoxy-compound, and melts at 225°. On further oxidation, the two preceding substances yield *trithiopentaoxybisacetylacetone,* $C_8H_{14}O_5S_3$, which crystallises from water and melts at 293°.

Trithiotrioxybismethylacetylacetone, $C_{10}H_{16}O_3S_3$, formed by oxidation of trithiobismethylacetylacetone, separates from alcohol in white crystals and melts at 255°.

Tetrathiotetraoxybisdimethylacetylacetone, $C_{14}H_{24}O_4S_4$, forms glistening, white crystals and decomposes at about 350°. G. Y.

Fermentation of Sugar without Enzymes. H. SCHADE (*Zeit. physikal. Chem.*, 1906, **57**, 1—46).—When an alkaline solution of dextrose is kept at a temperature rather above the ordinary, slow decomposition takes place, and the solution assumes a yellow or brown colour. If hydrogen peroxide has been added to the solution in sufficient quantity, no coloration is observed, even after the lapse of weeks; should there cease to be excess of hydrogen peroxide, the brown colour appears, but it can be destroyed if a little of the peroxide is added immediately after its appearance. It is shown that the brown colour is due to the action of alkali on acetaldehyde, which is produced in the decomposition of the sugar, and the preventive effect of the hydrogen peroxide consists in removing the acetaldehyde by oxidation to acetic acid. This view is in harmony also with experiments by Framm (Abstr., 1897, i, 5), and others by the author, which show that the production of the brown colour may be prevented also by (1) working under diminished pressure, and so removing the volatile aldehyde, (2) passing a rapid current of oxygen, hydrogen, or nitrogen through the solution, or (3) adding ammonia, sodium hydrogen sulphite, or potassium cyanide—substances which fix the aldehyde.

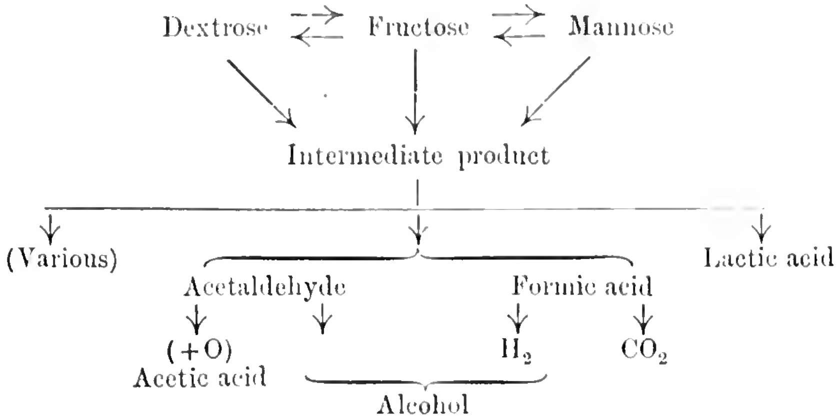
When such means are used to prevent the formation of a brown colour, the two products of the slow decomposition of the sugar (dextrose or lævulose) under the influence of alkali are formic acid and acetaldehyde. Other substances, for example, lactic acid, may be produced, but to an extent which is negligible so far as the main character of the decomposition is concerned.

For every molecule of sugar decomposed, two molecules of formic acid are produced, and it has further been shown, in a less direct manner, that for every molecule of sugar decomposed two molecules of acetaldehyde are produced. Thus the decomposition may be represented by the equation $C_6H_{12}O_6 = 2CH_3{\cdot}CHO + 2H{\cdot}CO_2H$. Galactose and mannose, although but few experiments have been made with them, appear to undergo a similar decomposition. The substances which were found to promote the sugar decomposition in question were potassium and sodium hydroxides, potassium, sodium and lithium carbonates, and disodium hydrogen phosphate. The decomposition is thus a catalysis by the OH' ion, and the velocity of decomposition is proportional to the concentration of that ion.

When a solution of sodium formate, slightly acidified with acetic acid and containing some finely-divided rhodium ("rhodium black") in suspension, is warmed under a reflux condenser, decomposition into carbon dioxide and hydrogen readily takes place. If, however, an amount of acetaldehyde equivalent to the sodium formate is distilled into the sodium formate solution while the latter is being heated, a yield of 60—70 per cent. of ethyl alcohol is obtained. That is, acetaldehyde and formic acid have reacted under the influence of a catalytic agent to form ethyl alcohol and carbon dioxide. Hence ethyl alcohol and carbon dioxide may be obtained from sugars by a purely chemical decomposition, and the change involved in fermentation may be realised without the intervention of enzymes.

The equation $C_6H_{12}O_6 = 2CH_3{\cdot}CHO + 2H{\cdot}CO_2H$ must not be regarded as excluding the possible formation of intermediate products, and in fact it is extremely probable that such are formed. Lactic acid is especially referred to in this connexion, and it is pointed out that, although only traces of this acid were found in the author's experiments, yet when the alkali concentration is high and the solutions are brown in colour considerable quantities are produced. It seems that the decomposition of the sugar (probably through some unknown intermediate product) takes place preferentially into aldehyde and formic acid, but that when this mode of decomposition is checked, possibly through accumulation of the decomposition products, other reactions take place; so, for example, in solutions containing a large quantity of hydroxyl ions, lactic acid is one of the chief products.

The following scheme represents diagrammatically the various possible courses of the sugar decomposition:



A detailed comparison of the purely chemical decomposition of the sugars with the alcoholic fermentation, the lactic acid fermentation, the acetic acid fermentation, and the formic acid fermentation shows that the latter processes are, so far as their end products are concerned, reproducible by agencies of a purely chemical nature. An enzyme is in fact only a catalytic agent of a special kind. J. C. P.

The Liquefaction of Starch Powder and Starch Grains. A. Boidin (*Compt. rend.*, 1906, **143**, 511—512).—Prior to Fernbach and Wolfe (this vol., i, 804) the author has shown that potassium hydrogen phosphate prevents the liquefaction of starch paste (compare Abstr., 1904, ii, 816), and in the present paper it is shown that whilst magnesium phosphate has a similar action, calcium phosphate does not render starch viscous, and if a solution of purified starch powder is heated in the presence of calcium sulphate or phosphate, it is saccharified to the extent of 33 per cent. Further, if the alkali hydrogen phosphates present in the starch granules are converted into calcium phosphate by the addition of calcium chloride, or into the corresponding di-hydrogen phosphate by the addition of acid, the solution obtained by boiling the starch grains is limpid and mobile and readily saccharified.

M. A. W.

Preparation of Methylamine from Ammonia and Methyl Sulphate. James Burmann (*Bull. Soc. chim.*, 1906, [iii], **35**, 801—803).—Commercial methyl sulphate is added in small portions at a time to excess of a 10 per cent. aqueous solution of ammonia cooled to −5°. The product is then added to excess of a 30 per cent. aqueous solution of sodium hydroxide and the mixture distilled, the issuing gas being passed into hydrochloric acid (20 per cent.). On evaporating, the ammonium chloride separates first and the methylamine hydrochloride ultimately obtained is purified by recrystallisation from boiling absolute alcohol. The yield is about 35 per cent. of the theoretical. T. A. H.

Liquid Methylamine as a Solvent, and a Study of its Chemical Reactivity. Harry D. Gibbs (*J. Amer. Chem. Soc.*, 1906, **28**, 1395—1422).—Liquid methylamine is a very good solvent for organic compounds, being better than liquid ammonia and probably better than methyl alcohol. For inorganic compounds, however, it is not so good a solvent as liquid ammonia, is far inferior to water, and seems to be approximately equal to methyl alcohol. The solubilities of various organic and inorganic substances have been studied as well as the reactions which sometimes take place.

The hydrocarbons are generally very soluble and the solid members crystallise readily from the solutions. The alcohols and phenols are also readily soluble. The following additive compounds are described. The phenol *compound*, $C_6H_5\cdot OH,2NH_2Me$, melts at 8·5—9·0°. The α-naphthol *compound*, $C_{10}H_7\cdot OH,2NH_2Me$, melts at about 37°. Quinol yields the *compounds*, $C_6H_4(OH)_2,8NH_2Me$,

$$C_6H_4(OH)_2,2NH_2Me,$$

and $C_6H_4(OH)_2,NH_2Me$, the last melting at 105°. Resorcinol gives the *compounds*, $C_6H_4(OH)_2,5NH_2Me$, $C_6H_4(OH)_2,2NH_2Me$, and $C_6H_4(OH)_2,NH_2Me$, the last of which melts at 95°. Pyrogallol furnishes the *compounds* $C_6H_3(OH)_3,3NH_2Me$ and

$$C_6H_3(OH)_3,2NH_2Me.$$

With phenolphthalein, the *compound*, $C_6H_4{:}C_2O_2{:}(C_6H_4\cdot OH)_2,2NH_2Me$ is obtained, and with alizarin, the *compound*,

$$C_6H_4{:}C_2O_2{:}C_6H_2(OH)_2,2NH_2Me,$$

is produced. On evaporating a solution of picric acid in liquid methylamine, a *substance* is obtained which decomposes without melting at 195°. Thymol yields a crystalline *substance* melting at 25°.

Acetaldehyde and benzaldehyde are miscible with liquid methylamine. *m*-Nitrobenzaldehyde is readily soluble and gives the *compounds*, $NO_2\cdot C_6H_4\cdot CHO,6NH_2Me$, melting at −9°, and

$$NO_2\cdot C_6H_4\cdot CHO,NH_2Me,$$

which melts and decomposes at 47°.

Acetone, acetophenone, and carbamide dissolve readily in liquid methylamine. Benzil is also very soluble and yields a *substance*, $COPh\cdot COPh,2NH_2Me$, which melts at about 23°. Quinone reacts with methylamine with development of heat and formation of a liquid which becomes successively green, purple and black. Anthraquinone is only slightly soluble.

The organic acids are generally very soluble, but in some cases insoluble methylamine salts are produced. The methylamine salts of several organic acids are described. The *acetate* melts at about 80°, the *palmitate* at 62°, the *succinate* at 150°, the *tartrate* at 148°, the *benzoate* at 110—112°, and the o-*nitrobenzoate* at 128—129°. Phthalic anhydride reacts with methylamine with development of heat and formation of a crystalline *substance*, which is probably *methylamine methylphthalamate*, $NHMe\cdot CO\cdot C_6H_4\cdot CO_2H,NH_2Me$. The *urate* decomposes without melting.

Chloroform mixes with liquid methylamine in all proportions and slowly reacts with it to form methylcarbimide and methylamine hydrochloride. Ethylene bromide reacts with methylamine with formation of a crystalline *substance*, which melts at 179° and is probably dimethylethylenediamine hydrobromide. Bromobenzene and *p*-bromoacetanilide dissolve freely without change.

Nitromethane is miscible with liquid methylamine and yields a crystalline *compound*, $CH_3 \cdot NO_2,NH_2Me$, which melts between $-8{\cdot}0°$ and $-7{\cdot}5°$. Nitrobenzene, *m*-dinitrobenzene, *o*-nitrotoluene, 2 : 4-dinitrotoluene, and 2 : 4-dinitroaniline are very soluble. 2 : 4 : 6-Trinitroaniline yields a red, crystalline *substance*.

Galactose and dextrose are soluble in liquid methylamine and furnish *compounds* of the composition $C_6H_{12}O_6,2NH_2Me$. Sucrose is also readily soluble.

Acetamide, phenylhydrazine, amyl formate, pyridine, azobenzene, *m*-nitrobenzenesulphonamide, and benzenesulphonimide are very soluble in liquid methylamine. Diphenylketoxime dissolves readily and yields the *compound*, $CPh_2{:}NOH,NH_2Me$, which decomposes a little below 140°.

Gallein and cœrulein furnish the *compounds* $C_{20}H_{12}O_7,3NH_2Me$ and $C_{20}H_{10}O_6,2NH_2Me$. Dichlorogallein and tetrachlorogallein yield products containing about 23 and 25 per cent. of methylamine respectively. Indigotin and rosaniline are readily soluble, whilst methyl orange is only slightly so.

The behaviour of a large number of inorganic salts with liquid methylamine is described. The sulphates are usually insoluble, whilst of the nitrates and haloids some are soluble and others insoluble. The following additive *compounds* are described: $CdI_2,4NH_2Me$, $AgNO_3,4NH_2Me$, and $AgNO_3,2NH_2Me$. Bismuth chloride, calcium chloride, chromic chloride, lithium chloride, lithium nitrate, lead nitrate, mercury methyl chloride. mercuric iodide, and probably cuprous chloride, cupric sulphate, mercurous chloride, and mercuric cyanide also form products containing methylamine of crystallisation.

E. G.

Compounds formed by the Action of Ammonia or Amines on Mercury Salts. Daniel Strömholm (*Arkiv Kem. Min. Geol.*, 1906, **2**, No. 23, 1—25).—The author classifies the definite compounds formed by ammonia or amines with mercury salts as follows: (*A*) Those in which Hg : X = 1 : 2; these are regarded as ammonia compounds. (*B*) Those in which Hg : X is greater than 1 : 2, and which are of the types: (1) with ammonia, $NH_2 \cdot HgX$, $Hg{:}N \cdot HgX$, and $Hg{:}N \cdot HgX + H_2O$; (2) with primary amines, $NHR \cdot HgX$ and $Hg(NR \cdot HgX)_2$. Compounds of the last type have not previously been prepared, although references have been made in the literature to ammonia derivatives of this type; the existence of the latter, however, the author was unable to confirm.

Working under the same conditions as Köhler (Abstr., 1880, 159, and *Ber.*, 1879, 12, 2321), the author was unable to obtain any of the three compounds of ethylamine and mercuric chloride described by this author. Instead, he obtained the *compound* $N_2Et_2Hg_3Cl_2$ as a white, amorphous mass.

Other compounds prepared from amines are: $NHEt_2,HgCl_2$, from diethylamine; $N_2Pr_2Hg_3Cl_2$, from propylamine; $N_2Me_2Hg_3Cl_2$, from methylamine. Compounds were also obtained from amylamine (Hg : Cl = 1·15 : 1) and benzylamine (Hg : Cl = 0·97 : 1).

The interaction of mercuric nitrate, ammonium nitrate, and ammonia in varying proportions, gave the diaminonitrate, aminonitrate, and nitrate of Millon's base, $NHg_2 \cdot OH$. T. H. P.

Preparation of Amino-alcohols. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 173610).—By the action of ammonia or organic bases on the β-substituted dihalogen hydrins, $OH \cdot CR(CH_2X)_2$, where X is a halogen, new alcohol bases are produced having the general formula $OH \cdot CR(CH_2 \cdot NYZ)_2$; these substances or their derivatives are of therapeutic importance owing to their property of dissolving uric acid.

Tetramethyldiaminodimethylethylcarbinol, $OH \cdot CEt(CH_2 \cdot NMe_2)_2$, prepared by heating β-ethyldichlorohydrin with aqueous dimethylamine at 180°, is a limpid oil boiling at 87° under 17 mm. pressure, which can be distilled under the ordinary pressure without decomposition; its *hydrochloride*, $OH \cdot CEt(CH_2 \cdot NMe_2)_2,HCl$, has a neutral reaction, and is a white, crystalline, hygroscopic substance. The hydriodide is also a well-defined salt.

Diaminodimethylethylcarbinol, $OH \cdot CEt(CH_2 \cdot NH_2)_2$, obtained in a similar manner, boils at 115° under 16 mm. pressure, and is very soluble in water.

Dianilinodimethylethylcarbinol, $OH \cdot CEt(CH_2 \cdot NHPh)_2$, prepared by heating β-ethyldibromohydrin and aniline at 200°, is a yellow oil having an odour of quinoline and boiling at 145—148° under 17 mm. pressure.

Tetramethyldiaminophenyldimethylcarbinol, $OH \cdot CPh(CH_2 \cdot NMe_2)_2$, formed by condensing β-phenyldichlorohydrin with aqueous dimethylamine at 180°, is a yellow oil with a basic odour; it boils at 139·5° under 11 mm. pressure.

Dipiperidyldimethylethylcarbinol, $OH \cdot CEt(CH_2 \cdot C_5NH_{10})_2$, is a viscid, colourless oil boiling at 174° under 16 mm. pressure.

Dimethylaminodiethylaminodimethylethylcarbinol,

$$OH \cdot CEt(CH_2 \cdot NMe_2) \cdot CH_2 \cdot NEt_2,$$

is a colourless liquid boiling at 107° under 16 mm. pressure.

G. T. M.

Preparation of Diaminoalkyl Esters. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 173631. Compare preceding abstract). —*Tetramethyldiaminodimethylethylcarbinyl benzoate*,

$$OBz \cdot CEt(CH_2 \cdot NMe_2)_2,$$

produced by the Schotten-Baumann reaction from tetramethyldiaminodimethylethylcarbinol, forms a *hydrochloride*,

$$OBz \cdot CEt(CH_2 \cdot NMe_2)_2,HCl,$$

separating in white crystals and melting at 169°.

Tetramethyldiaminophenyldimethylcarbinyl benzoate hydrochloride, $OBz \cdot CPh(CH_2 \cdot NMe_2)_2,HCl$, produced by benzoylating the corresponding carbinol with benzoyl bromide in pyridine and combining the resulting benzoate with hydrogen chloride (1 mol.), is a white, crystalline powder melting at 187°.

Tetramethyldiaminodimethylethylcarbinyl iso*valerate*,

$$CHMe_2 \cdot CH_2 \cdot CO \cdot O \cdot CEt(CH_2 \cdot NMe_2)_2,$$

prepared by treating the corresponding carbinol with *iso*valeryl chloride and sodium hydroxide, is a colourless liquid boiling at 137°

under 16 mm. pressure and having a faint aromatic and basic odour.

Tetramethyldiaminodimethylethylcarbinyl ethyl carbonate, obtained from the corresponding carbinol and ethyl chlorocarbonate, is a colourless oil boiling at 129° under 17 mm. pressure; the *hydrochloride* is a white, crystalline powder which melts at 160°.

Tetramethyldiaminodimethylethylcarbinyl cinnamate,

$$CHPh:CH\cdot CO_2\cdot CEt(CH_2\cdot NMe_2)_2,$$

is a viscid, colourless oil; its *monohydrochloride* is a white, crystalline powder having a neutral reaction in aqueous solution. This salt produces an anæsthetic effect, lasting twice as long as that brought about by the same quantity of cocaine. G. T. M.

Copper and Nickel Salts of Certain Amino-acids. ALESSANDRO CALLEGARI (*Gazzetta*, 1906, **36**, ii, 63—67. Compare Bruni and Fornara, Abstr., 1904, i, 855; 1905, i, 263; Ley, Abstr., 1905, i, 175).—The *copper* salt of β-aminopropionic acid (β-alanine), prepared by warming the acid with freshly precipitated copper hydroxide, has the properties of an ordinary copper salt and not those of a cuprammonium derivative (*loc. cit.*); the cuprammonium or nickelammonium salts appear to be formed only from α-amino-acids. *Copper aminosulphonate*, $(NH_2\cdot SO_2\cdot O)_2Cu,2H_2O$, prepared by dissolving copper carbonate in an aqueous solution of aminosulphonic acid, forms microscopic, blue crystals and is an ordinary copper salt; the *nickel* salt, $(NH_2\cdot SO_3)_2Ni,4H_2O$, is similar. The copper salt of hydrazinecarboxylic acid (Stollé and Hofmann, Abstr., 1905, i, 28) is apparently a cuprammonium salt, as it has the intense violet colour characteristic of such salts; it cannot be isolated, as it rapidly decomposes, giving metallic copper. The *nickel* salt, $(NH_2\cdot NH\cdot CO_2)_2Ni$, can be isolated, and is a nickelammonium salt; its solution is intensely blue and does not respond to the usual tests for nickel. W. A. D.

Optically Active αβ-Diaminopropionic α- and β-Thioglyceric Acids. CARL NEUBERG and ERICH ASCHER (*Chem. Centr.*, 1906, ii, 1119; from *Biochem. Zeit.*, 1906, **1**, 380—382).—The racemic variety of αβ-diaminopropionic acid can be split into its optically active constituents by the fractional crystallisation of its salt with *d*-camphorsulphonic acid; in this way the dextro-variety can be obtained practically pure. The sulphate of the latter is converted by barium nitrite into *l*-glyceric acid, from which it follows that dextrorotatory αβ-diaminopropionic acid is in reality a lævo form. The *hydrochloride* of *l*-diaminopropionic acid is dextrorotatory; it forms a copper salt, $(C_3H_7O_2N_2)_2Cu,H_2O$. When proteincystin is treated in sulphuric acid solution with barium nitrite, it is converted into αβ-thioglyceric acid which has $[\alpha]_D$ −10·6° (approx.); its *barium* salt, $(C_3H_4O_3S)_2Ba$, has $[\alpha]_D$ −19·08°. A solution of the barium salt gives heavy precipitates with mercuric chloride, lead, or copper acetates. Zinc and hydrochloric acid reduce the disulphide to *β-thioglyceric acid*, a substance which, with lead, copper, or iron salts, gives colour reactions similar to those of cystein. In preparing the inactive αβ-diaminopropionic acid from αβ-dibromopropionic acid and ammonia, 10 per cent. of the dibromo-acid is converted into *iso*serine. Cystin, on dry distillation, loses carbon dioxide, giving *diaminoethylene disulphide*, which was isolated in the form of a picrate. P. H.

Reduction of Oximino-Esters. Synthesis of a New Leucine. Louis Bouveault and René Locquin (*Bull. Soc. chim.*, 1906, [iii], **35**, 965—969).—Most of the facts recorded in this paper have already been given (Abstr., 1905, i, 636).—When ethyl α-oximino-β methylvalerate is reduced with sodium amalgam in a cold alcoholic solution, only 35 per cent. of the theoretical yield of ethyl α-amino-β-methylvalerate is obtained, but a 60 per cent. yield may be secured by effecting the reduction with zinc dust and alcohol saturated with hydrogen chloride. From this amino-ester the corresponding acid (Ehrlich's *iso*leucine, Abstr., 1904, i, 560) may be obtained by agitating its solution in ether with a dilute aqueous solution of sodium hydroxide. The acid yields a p-toluenesulphonate which melts at 139°, and when warmed with formic acid (compare Fischer and Warburg, Abstr., 1906, i, 72) furnishes the formyl derivative, $\mathrm{CHMeEt{\cdot}CH(NH{\cdot}CHO){\cdot}CO_2H}$, which crystallises from boiling water and melts at 121—122°. The amino-acid prepared in this way is racemic.

With benzoyl chloride in cooled pyridine solution, ethyl α-amino*iso*hexoate forms a *benzoyl* derivative, which crystallises from a mixture of alcohol and light petroleum, melts at 79°, and boils at 211° under 15 mm. pressure. T. A. H.

Additive Compounds of Dicyanodiamide and Inorganic Salts. Hermann Grossmann and Bernhard Schück (*Ber.*, 1906, **39**, 3591—3593).—The *compound* $\mathrm{CuSO_4,2C_2H_4N_4,4H_2O}$, formed by heating copper sulphate with dicyanodiamide in aqueous solution on the water-bath, is obtained as a light blue, thick, crystalline precipitate which becomes dark green when dried at 125°; the filtrate yields only green, basic products of varying composition. The *compound* $\mathrm{CdSO_4,2C_2H_4N_4,2H_2O}$ crystallises in short, colourless prisms, effloresces on exposure to air, and is more soluble in water than is the copper compound. The mercuric compound $\mathrm{HgCl_2,C_2H_4N_4}$, crystallises in glistening, pointed needles. The copper and cadmium compounds belong to Werner's co-ordinated types $(\mathrm{MA_6})\mathrm{X_2}$ and $\left(\mathrm{M.}\genfrac{}{}{0pt}{}{\mathrm{A_4}}{\mathrm{X_2}}\right)$, whilst the mercuric compound is only incompletely co-ordinated. G. Y.

Oxidation of Uric Acid in the presence of Ammonia. Gustav Denicke (*Annalen*, 1906, **349**, 269—298).—*Iminoallantoin*, $\mathrm{C_4H_7O_2N_5}$, obtained when finely divided uric acid, suspended in ammonium hydroxide at 0°, is oxidised by one atomic proportion of oxygen derived from potassium permanganate or ferricyanide, separates from hot water in elongated crystals, darkens at 210°, and carbonises at 295° without melting, is soluble in mineral acids, yields oxalic acid with warm potassium hydroxide, and in acid solution or by prolonged boiling with water is converted into allantoin. The resolution into its active components is not effected by tartaric acid.

When the oxidation is performed under similar conditions with potassium ferricyanide (2 atoms of oxygen), crystals of a *substance*, $C_4H_{10}O_3N_6(A)$, are precipitated, whilst from the filtrate a *substance*, $C_4H_8O_2N_6(B)$, is obtained; the latter only is formed when the oxidation is effected with more concentrated ammonium hydroxide at the ordinary temperature. The substance *A* darkens at 108° and is carbonised at 295°, dissolves in cold water to an alkaline solution which decomposes by warming, and changes into *B* when digested with ammonium hydroxide. It is soluble in a small quantity of cold concentrated hydrochloric acid (parabanic acid is obtained by warming), and from the solution a *substance*, $C_4H_5O_2N_5$, separates; by saturating the solution with ammonia, oxaluric acid is obtained. With alcoholic hydrogen iodide at −7°, an easily decomposable *hydriodide*,

$$C_4H_{10}O_3N_6,HI,$$

is formed.

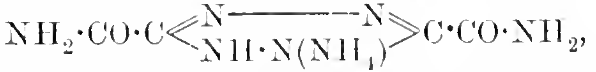
The substance *B* forms microscopic prisms, darkens at 200°, forms a neutral solution in water, and is decomposed by hydrochloric acid, yielding ultimately parabanic acid.

Both *A* and *B* are decomposed by potassium hydroxide, forming urea and a *substance* the composition of which approximates to that of di-iminoparabanic acid, $C_3H_4ON_4$; this substance is a white powder which darkens at 195°, forms a crystalline *potassium* derivative, and by acids is converted into parabanic acid.

The evidence for the formulæ of these substances is discussed.

C. S.

Pseudodiazoacetamide. THEODOR CURTIUS, AUGUST DARAPSKY, and ERNST MÜLLER (*Ber.*, 1906, **39**, 3410—3437. Compare Curtius, Abstr., 1885, 883; Hantzsch and Silberrad, Abstr., 1900, i, 261; Silberrad, Trans., 1902, **81**, 601).—The ammonium salt of pseudodiazoacetamide is represented by the formula



$$NH_2{\cdot}CO{\cdot}C{<}\genfrac{}{}{0pt}{}{N\text{———————}N}{NH{\cdot}N(NH_4)}{>}C{\cdot}CO{\cdot}NH_2,$$

and is most readily prepared by the action of liquid ammonia on ethyl diazoacetate; no diazoacetamide is formed, and only a very small amount of bisdiazoacetamide, which is readily removed. When warmed with water, pseudodiazoacetamide yields one-third of its nitrogen in the gaseous form, one-third as hydrazine, which was estimated as benzylideneazine, and the remainder as glyoxylamide, which was isolated in the form of its phenylhydrazone (Krückeberg, Abstr., 1894, i, 369). Carbon dioxide and oxalic acid do not appear to be formed, although both are produced when pseudodiazoacetamide is boiled with dilute acids.

The *azine* of *glyoxylamide*, $NH_2{\cdot}CO{\cdot}CH{:}N{\cdot}N{:}CH{\cdot}CO{\cdot}NH_2$, is obtained as an intermediate product when pseudodiazoacetamide is warmed with water at 60—70° in small quantities until nitrogen ceases to be evolved and the solution cooled to 0°. It crystallises in small, pale yellow needles, melts at 202°, is soluble in warm water, but insoluble in alcohol or ether, and is readily hydrolysed, even in the cold, by dilute acids.

Pseudodiazoacetamide is converted into bisdiazoacetamide when warmed with dilute sodium hydroxide solution, more slowly with the cold alkali, and also when warmed with ammonium hydroxide.

When an aqueous solution containing the ammonium salt of pseudodiazoacetamide and sodium nitrite is acidified, a bluish-red precipitate of 1 : 2 : 4 : 5-*tetrazine*-3 : 6-*dicarboxylamide*,

$$NH_2\cdot CO\cdot C\lessdot\genfrac{}{}{0pt}{}{N\cdot N}{N:N}\gtrdot C\cdot CO\cdot NH_2,$$

is obtained. It is insoluble in all ordinary solvents, and when heated turns brown at 210° and is quite black at 280°. When warmed with water, nitrogen is evolved and the colour disappears. The same amide may be obtained by the oxidation of bisdiazoacetamide with nitric acid; when reduced with hydrogen sulphide, it yields bisdiazoacetamide.

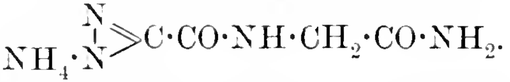
The *oxamic acid hydrazone* of *glyoxylamide*,

$$NH_2\cdot CO\cdot CO\cdot NH\cdot N{:}CH\cdot CO\cdot NH_2,$$

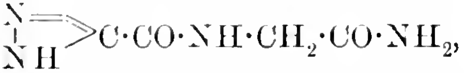
is obtained when tetrazinedicarboxylamide is boiled with water. It forms a pale yellow, crystalline powder, is insoluble in all ordinary solvents, turns brown at 270°, but is not molten at 300°, and when boiled with dilute sulphuric acid yields semioxamazide (Kerp and Unger, Abstr., 1897, i, 270) together with glyoxylic acid.

The acid previously obtained by Hantzsch and Lehmann (Abstr., 1901, i, 132) and termed bisazoxyacetic acid is now shown to be 1 : 2 : 4 : 5-*tetrazine*-3 : 6-*dicarboxylic acid*. J. J. S.

Action of Ammonia on Ethyl Diazoacetylglycine. (*iso*-Diazoacetylaminoacetic Acid). II. Theodor Curtius and James Thompson (*Ber.*, 1906, 39, 3398—3409).—The product previously (this vol., i, 404) described as an azomethane derivative is shown to be the *ammonium* salt of iso*diazoacetylglycinamide*,



$$\genfrac{}{}{0pt}{}{N}{NH_4\cdot N}\!\!\gtrdot C\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH_2.$$

This ammonium salt is stable, and does not lose ammonia when kept, but is strongly dissociated in aqueous solution; with cold aqueous hydrochloric acid, it gives up 1 mol. of ammonia, and with hot concentrated acid or alkali 2 mols. The ammonium salt reacts with benzoyl chloride and sodium hydrogen carbonate solution, yielding *benzoyl*iso*diazoacetylglycinamide*, $N_2H{:}C\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot COPh$, which crystallises from acetone in slender, colourless needles and melts and decomposes at 185°. The corresponding *acetyl* derivative, $C_6H_8O_3N_4$, crystallises from alcohol in colourless needles and melts and decomposes at 158°. When boiled with water or alcohol, it is hydrolysed. The *silver* salt, $N_2Ag{:}C\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH_2$, obtained by precipitating a solution of the ammonium salt with silver nitrate, forms slender needles, and may be recrystallised from hot water. iso-*Diazoacetylglycinamide*,  $\genfrac{}{}{0pt}{}{N}{NH}\!\!\gtrdot C\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH_2$, obtained by suspending the silver salt in water, passing in hydrogen sulphide, and evaporating the clear solution under reduced pressure, forms glistening prisms melting and decomposing at 154—155°. It is hygroscopic, and explodes when rapidly heated. It dissolves readily in water, sparingly in alcohol, and is insoluble in ether, acetone, or chloroform. Its aqueous solution is decidedly acid and decolorises bromine water; when heated with concentrated hydrochloric acid it yields nitrogen (1 mol.) and ammonia (1 mol.). It yields the same benzoyl and acetyl derivatives as are obtained from the ammonium salt. When the ammonium salt is heated with concentrated hydrochloric acid at 130—140° it yields nitrogen, chloroacetic acid, and glycollic acid. When boiled with normal sodium hydroxide solution for an hour, evaporated under reduced pressure, and decomposed at 0° with the theoretical amount of concentrated hydrochloric acid, it yields iso*diazoacetylaminoacetic acid*,  $\begin{matrix}N= \\ | \\ NH\end{matrix}\!>\!C{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2H$, in the form of a white, crystalline precipitate, readily soluble in warm water, from which it crystallises in anisotropic, rhombic prisms. The same compound is formed by hydrolysing the ester with sodium hydroxide solution. It possesses both acid and basic properties. The *hydrochloride* forms a crystalline mass melting at 151°. The free acid when slowly heated decomposes at 169—170°.

A considerable amount of potassium cyanide is formed when ammonium *iso*diazoacetylglycinamide is fused with potassium hydroxide. J. J. S.

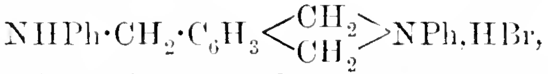
Remarkable Formation of Alkyl Derivatives of Mercury. Julius Tafel (*Ber.*, 1906, **39**, 3626—3631).—Considerable amounts of mercury *sec.*-butyl are formed when methyl ethyl ketone is reduced electrolytically in the presence of mercury cathodes. The maximum yields are obtained at a temperature of 45—50°. The cathode liquid consists of the ketone with some thirteen times its weight of 30 per cent. sulphuric acid, and a voltage of 7·6 to 8·4 for a current of 25 amperes is employed. After some two hours, the amount of crude mercury compound is 1·3 times the weight of ketone used. After several distillations in high vacua, the *mercury* sec.*-butyl*, $Hg(C_4H_9)_2$, is obtained as a colourless oil boiling at 46° under very low pressures, and a considerable residue of another mercury compound in the form of a yellow oil is left. The mercury butyl boils at 91—93° under 15 mm. pressure, and readily reacts with iodine, yielding *sec.*-butyl iodide and mercury butyliodide. J. J. S.

The Study of Hydroaromatic Substances. Edward Divers, Arthur W. Crossley, William H. Perkin, jun., Martin O. Forster, and Henry R. Le Sueur (*Brit. Assoc. Rep.*, 1905, 153.).—A report on the production of hydroaromatic substances from the aromatic hydrocarbons, phenols, amines, ketones, and acids. Reference is also made to the nature of double linkings. G. T. M.

Fluoro-aromatic Compounds. Arnold F. Holleman (*Rec. trav. chim.*, 1906, [ii], **25**, 330—333).—*o*- and *p*-Fluoroacetanilides prepared by reducing the crude fluoronitrobenzene (M. Holleman, Abstr., 1905, i, 424) and acetylating the product, can be separated by repeated fractional crystallisation from benzene and light petroleum; o-*fluoroacetanilide* melts at 80°, and p-*fluoroacetanilide* at 150°.

p-Fluorotoluene (Holleman and Beckman, Abstr., 1904, i, 232) freezes in a mixture of solid carbon dioxide and alcohol, whilst the ortho- and meta-isomerides remain liquid. "Fluoro-saccharin" (De Roode, Abstr., 1891, 1226) can be prepared from *p*-fluorotoluene by converting it into *p-fluorotoluenesulphonic chloride*, which boils at 145—150° under 20 mm. pressure and yields the corresponding sulphonamide melting at 140° (De Roode gives 155°) on treatment with ammonium carbonate; this can be oxidised by potassium permanganate to "fluoro-saccharin" melting at 200°. M. A. W.

Action of Bromine on ψ-Cumene. ROBERTO CIUSA (*Gazzetta*, 1906, **36**, ii, 90—93. Compare Schramm, Abstr., 1886, 451; Hjelt and Gadd, *ibid.*, 615).—*Tri-ω-bromocumene*, $C_6H_3(CH_2Br)_3$, obtained by adding bromine (3 mols.) to ψ-cumene exposed to direct sunlight, and subsequently heating at 160°, crystallises from light petroleum in white, lustrous needles and melts at 154°. Its structure follows from its yielding with aniline in alcoholic solution 6-*anilinomethyl*-2-*phenyldihydroisoindole hydrobromide*,



$$NHPh\cdot CH_2\cdot C_6H_3{<}{}^{CH_2}_{CH_2}{>}NPh,HBr,$$

which crystallises from light petroleum and melts at 132°; the *base*, $C_{21}H_{20}N_2$, also crystallises from light petroleum and melts at 128°. W. A. D.

Derivatives of *tert.*-Butylbenzene. EYVIND BŒDTKER (*Bull. Soc. chim.*, 1906 [iii], **35**, 825—836. Compare Abstr., 1904, i, 801).—p-*Chloro*-tert.-*butylbenzene*, obtained by condensing chlorobenzene with *tert.*-butyl chloride or *iso*butyl chloride in presence of aluminium chloride, is a limpid liquid with an aromatic odour, boils at 211° (corr.) under 759 mm. pressure, has a sp. gr. 1·0675 at 18·5°/4° and n_D 1·51230 at 20°. On oxidation with chromic acid it furnishes *p*-chlorobenzoic acid. It dissolves in fuming nitric acid, yielding a mixture of 4-*chloro*-2:3-*dinitro*-tert.-*butylbenzene* and 4-*chloro*-3:5-*dinitro*-tert.-*butylbenzene*. The first of these is a yellow, crystalline powder and melts at 94—95°, and the second crystallises in hexagonal tablets, large, prismatic needles, or small prismatic grains and melts at 116—117°. When *iso*butyl chloride is condensed with bromobenzene in presence of aluminium chloride, the principal fraction is a *product* boiling at 225—226° at atmospheric, or at 110—111° under 15 mm. pressure, and only a small quantity of *p*-bromo-*tert.*-butylbenzene is obtained. This boils at 232—233° (compare Schramm, Abstr., 1889, 127). The nature of the fraction boiling at 225—226° has not been definitely ascertained. On oxidation with chromic acid it furnishes *p*-bromobenzoic acid, and on solution in fuming nitric acid yields a mixture of 4-*bromo*-2:3-*dinitro*-tert.-*butylbenzene* and 4-*bromo*-3:5-*dinitro*-tert.-*butylbenzene*. The first of these is a yellow, crystalline powder and melts at 92—93°, and the second forms slender, almost colourless, needles and melts at 136°.

p-Iodo-*tert.*-butylbenzene, obtained together with di-iodobenzene (Dumreicher, Abstr., 1883, 53) when *iso*butyl chloride is condensed with iodobenzene in presence of ferric chloride, boils at 253—254°

(corr.) under 766 mm. pressure, has a sp. gr. 1·4392 at 14°/4°, and n_D 1·57076 at 20°, and does not liberate iodine on exposure to light (compare Pahl, Abstr., 1884, 1009, and Bialobrzeski, *ibid.*, 1897, i, 514). On oxidation with chromic acid, it yields *p*-iodobenzoic acid (m. p. 236°; compare Glassner, Abstr., 1875, 888). On nitration, it liberates some iodine and furnishes (*a*) 4-*iodo*-2 : 3-*dinitro*-tert.-*butylbenzene*, which crystallises in lemon-yellow leaflets and melts at 110—111°, and (*b*) a *substance* forming colourless prismatic crystals, melting at 243° which may be a di-iodonitrobutylbenzene. When the parent substance is treated with a great excess of fuming nitric acid *p*-iodonitrobenzene is formed.

When *iso*butyl chloride is condensed with cumene in presence of aluminium chloride, *tert.*-butylbenzene, *p*-di-*tert.*-butylbenzene and propyl chloride are produced. An attempt to separate the constituents of this mixture by Radziewanowski's process (Abstr., 1895, i, 129) gave only a tarry product, which boiled above 300° and decomposed.

When *iso*amyl chloride is condensed with *tert.*-butylbenzene in presence of aluminium chloride, *p*-di-*tert.*-butylbenzene is produced and the *iso*amyl chloride can be recovered unaltered (compare Baur, Abstr., 1894, i, 445). The hydrocarbon, when dissolved in fuming nitric acid, furnishes 2 : 6-*dinitro*-1 : 4-*di*-tert.-*butylbenzene*, which crystallises from boiling alcohol in slender, colourless needles and melts at 190—191° (corr.). Indications of the presence of an *o*-dinitro-derivative in the mother liquors from the crystallisation of the *m*-dinitro-derivative were obtained.

The dinitro-derivatives obtained from *p*-dibutylbenzene by Verley (Abstr., 1899, i, 424) and Baur (Abstr., 1894, i, 445) are probably impure.

T. A. H.

The Transformation of Aromatic Nitroamines and Allied Substances, and its Relation to Substitution in Benzene Derivatives. FREDERIC S. KIPPING, KENNEDY J. P. ORTON, SIEGFRIED RUHEMANN, ARTHUR LAPWORTH, and JOHN T. HEWITT (*Brit. Assoc. Rep.*, 1905, 103).—A report on the transformation of symmetrically trisubstituted aromatic nitroamines and diazonium hydroxides and on the action of light on solutions of certain diazonium salts.

G. T. M.

Combination of Magnesium Bromide with Certain Amines. VIII. BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, i, 5).—Aniline reacts with magnesium bromide with development of much heat, giving three compounds. The equilibrium curve of the system magnesium bromide–aniline consists of three branches, representing (1) the solubility of the *compound*, $MgBr_2,6NH_2Ph$ in aniline and ending at 103°; (2) the solubility of the *compound* $MgBr_2,4NH_2Ph$ and ending at 237°; (3) probably the *compound* $MgBr_2,2NH_2Ph$, or $MgBr_2,NH_2Ph$, but owing to the setting in of decomposition, the investigation could not be carried beyond 250—260°. Phenylhydrazine also gives the *compound* $MgBr_2,6N_2H_3Ph$, and its solubility curve corresponds closely with that of the aniline compound in aniline. The first curve ends at 99°, but owing to decomposition the second was only observed up to 200°. It probably corresponds with the *compound* $MgBr_2,4N_2H_3Ph$. Z. K.

Cyanoacetylchloroanilines and the corresponding Oxamic Acids. Galeazzo Piccinini and A. Delpiano (*Atti R. Accad. Sci. Torino*, 1906, 41, 1005—1018).—The three chloroanilines react with ethyl cyanoacetate yielding the corresponding chloro-derivatives of cyanoacetylaniline: $NH_2{\cdot}C_6H_4Cl + CN{\cdot}CH_2{\cdot}CO_2Et =$

$$CN{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4Cl + Et{\cdot}OH.$$

m-*Chlorocyanoacetylaniline*, C_9H_7ONCl, prepared from *m*-chloroaniline and ethyl cyanoacetate, crystallises from aqueous alcohol in white, nacreous plates melting at 142° (corr.), dissolves readily in acetone and sparingly in ether or benzene, and is hydrolysed either by dilute alkali solution or, more slowly, by boiling with water.

o-*Chlorocyanoacetylaniline* crystallises from aqueous alcohol in small, colourless prisms or slender, silky needles melting at 125° and resembles the corresponding meta-compound in its behaviour towards solvents and hydrolytic agents.

p-*Chlorocyanoacetylaniline* crystallises from aqueous alcohol in shining, colourless prisms which aggregate in the form of plates having a silvery lustre; it melts at 204° and behaves towards solvents and hydrolysis like its isomerides.

When oxidised by means of a large excess of permanganate, these compounds yield, almost quantitatively, the corresponding chlorophenyloxamic acids, according to the equation: $C_6H_4Cl{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}CN + O_2 = C_6H_4Cl{\cdot}NH{\cdot}CO{\cdot}CO_2H + HCN$.

p-*Chlorophenyloxamic acid*, $C_6H_4Cl{\cdot}NH{\cdot}CO{\cdot}CO_2H$, crystallises from absolute or aqueous alcohol with 1Et·OH in colourless prisms which melt at 190—191° and effloresce in the air; it dissolves readily in acetone and sparingly in chloroform or benzene. The *potassium*, *silver*, *barium*, *ferric*, *mercurous*, and *lead* salts are described.

o-*Chlorophenyloxamic acid* crystallises with H_2O from aqueous alcohol in colourless, prismatic needles and melts at 93—95°; the anhydrous acid melts at 136—137°. The *potassium*, *silver*, *calcium*, *barium*, *copper*, and *mercurous*, *lead*, and *ferric* salts are described.

m-*Chlorophenyloxamic acid* crystallises from water with $1\frac{1}{2}H_2O$ in shining needles melting at 90—100°, whilst the anhydrous acid melts at 144—145°; the acid dissolves much more readily than its isomerides in water and is soluble in 95 per cent. alcohol or acetone and sparingly so in benzene or chloroform. The *potassium* salt forms nacreous, anhydrous leaflets.

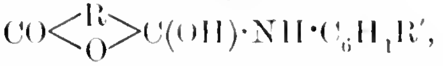
These three acids exhibit a strong acid reaction in aqueous solution and are monobasic towards alkali hydroxides, using phenolphthalein as indicator. T. H. P.

Action of Phenylcarbimide on certain Phenylamic Acids. Gino Abati and Paolo Gallo (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1906, [iii], 12, 291—299).—The authors have examined the behaviour of phenylcarbimide towards solutions, in non-dissociating solvents, of phenylphthalamic, *p*-tolylphthalamic, *d-cis*-phenylcamphoramic and *p*-ethoxyphenylmaleinamic acids. With the exception of the phenylcamphoramic acid, all the acids are resolved into the corresponding anhydrides and aniline, the latter combining with the phenylcarbimide to form diphenylcarbamide.

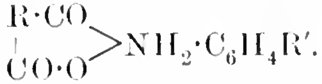
This result indicates that these acids have the structure

$$CO_2H{\cdot}R{\cdot}CO{\cdot}NH{\cdot}C_6H_4R'$$

rather than $CO_2H{\cdot}R{\cdot}C(OH){:}N{\cdot}C_6H_4R'$ or



$$CO{<}\overset{R}{\underset{O}{}}{>}C(OH){\cdot}NH{\cdot}C_6H_4R',$$

since the last two formulæ contain an alcoholic hydroxyl, which would be capable of reacting with the phenylcarbimide. The non-reactivity of *d-cis*-phenylcamphoramic acid with phenylcarbimide points to its having the constitution  $\begin{matrix}R{\cdot}CO\\ |\\ CO{\cdot}O\end{matrix}{>}NH_2{\cdot}C_6H_4R'$.

In the cases of the above acids which react with phenylcarbimide, a deep yellow substance, readily soluble in ether, is formed in amount too small to allow of its investigation. T. H. P.

Cinnamylamine ("Styrylamine") Bases and their Relation to Ephedrine and ψ-Ephedrine. [ERNST SCHMIDT] and HERMANN EMDE (*Arch. Pharm.*, 1906, **244**, 269—299).—Cinnamylamine hydrochloride (E. Schmidt and Flaecher, Abstr., 1905, i, 371) melts at 236°; the *aurichloride* and *mercurichloride* melt at 138—139° and 189° respectively. When the amine is boiled with excess of acetyl chloride it is converted into *cinnamylacetamide*,

$$CHPh{:}CH{\cdot}CH_2{\cdot}NHAc,$$

which melts at 87·5°. It reacts with methyl iodide in methyl-alcoholic solution at the ordinary temperature; quaternary *cinnamyltrimethylammonium iodide*, melting at 178°, is practically the only product, but much of the amine remains unchanged; the corresponding quaternary *aurichloride* and *platinichloride* melt at 185° and 232—234° respectively.

Cinnamyltrimethylamine (Abstr., 1905, i, 370), aurichloride, platinichloride, *mercurichloride*, $(C_{12}H_{18}N)_2HgCl_4,\frac{1}{2}HgCl_2$, and *picrate* (not analysed) melt at 185°, 228—230°, 171°, and 159° respectively. With methylamine in alcoholic solution at the ordinary temperature cinnamyl chloride in part condenses to form *cinnamylmethylamine hydrochloride*, $CHPh{:}CH{\cdot}CH_2{\cdot}NHMe,HCl$; this and the corresponding *platinichloride*, *aurichloride*, *mercurichloride*, $C_{10}H_{13}N,HHgCl_3$, and *picrate* (not analysed) melt at 151·5°, 212°, 103°, 166°, and 147° respectively. When cinnamyl chloride is warmed with pyridine, *cinnamylpyridine hydrochloride*, $CHPh{:}CH{\cdot}CH_2{\cdot}C_5NH_4,HCl$, is formed; the corresponding *platinichloride*, *aurichloride*, and *picrate* (not analysed) melt at 220—222°, 101·5°, and 146° respectively.

Cinnamyltrimethylamine hydrochloride does not yield additive compounds with hydrogen bromide or iodide in aqueous solution, neither does cinnamylamine hydrochloride take up hydrogen when treated in aqueous alcoholic solution with sodium amalgam. Cinnamyltrimethylamine hydrochloride, however, in aqueous solution is attacked by sodium amalgam: it is decomposed almost quantitatively into α-phenylpropylene, $CHPh{:}CH{\cdot}CH_3$, and trimethylamine hydrochloride, so that the reaction can be used advantageously for the preparation of α-phenylpropylene.

Neither cinnamylamine nor cinnamylmethylamine hydrochloride forms a chlorohydrin when treated with hypochlorous acid (aqueous sodium hypochlorite). Cinnamyltrimethylamine hydrochloride does form a *chlorohydrin*, presumably $OH\cdot CHPh\cdot CHCl\cdot CH_2\cdot NMe_3Cl$, of which the *platinichloride* and *aurichloride* melt respectively at 210—212° and 130—132°; the yield is not quantitative, however. This chlorohydrin is hardly affected by zinc and dilute sulphuric acid, but sodium amalgam does remove the chlorine, forming a quaternary ammonium base, $OH\cdot CHPh\cdot CH_2\cdot CH_2\cdot NMe_3\cdot OH$, of which the *aurichloride* and *platinichloride* melt at 103° and 216—218° respectively (a little of this base is formed when cinnamyltrimethylamine chloride is treated with aqueous hydrogen iodide).

As this quaternary base is not identical with either of those prepared by the methylation of ephedrine and ψ-ephedrine respectively, neither of the latter substances can have the formula,

$$OH\cdot CHPh\cdot CH_2\cdot CH_2\cdot NHMe.$$

C. F. B.

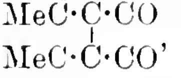
Condensation of Ethyl Acetoacetate and Phenylcarbamide.

WALTHER KIESSLING (*Annalen*, 1906, **349**, 299—323).—Phenylcarbamide, unlike carbamide, thiocarbamide, or guanidine, condenses with ethyl acetoacetate in the presence of ether, to form not ethyl phenyluraminocrotonate (compare Behrend and Meyer, Abstr., 1901, i, 136), but a yellow oil having the composition $C_{13}H_{16}O_3N_2$ (compare Behrend, Abstr., 1886, 443), the most suitable temperature being 133—134°. The oil, the mean molecular weight of which by the ebullioscopic method is 174·7, is decomposed by cold 5 per cent. hydrochloric acid or by alcohol, giving a yield of ethyl phenylcarbamate in accordance with the equation: $C_{13}H_{16}O_3N_2 + 2H_2O = NHPh\cdot CO_2Et + NH_3 + CO_2 + COMe_2$; the carbamate is also obtained by inoculating the oil at 0° with a crystal of the ester.

For these reasons, the substance is regarded as an easily dissociable compound or possibly a mixture:

$$2C_{13}H_{16}O_3N_2 = 2NHPh\cdot CO_2Et + C_8H_{10}O_2N_2.$$

The hypothetical substance, $C_8H_{10}O_2N_2$, has not been isolated, but is regarded as containing the skeleton,



$$\begin{array}{l}\text{MeC·C·CO}\\ \qquad\;\;|\\ \text{MeC·C·CO}\end{array}$$

, since the yellow oil and phenylhydrazine yield Knorr's bisphenylmethylpyrazolone.

Methylcarbamide reacts with ethyl acetoacetate at 125—127° in the presence of ether to form a *substance* which has the composition, but not the properties of ethyl methylaminocrotonate, $C_7H_{13}O_2N$.

Diphenylcarbamide, ethyl acetoacetate, and ether react at 154° to form a reddish-brown oil (compare Behrend, *Annalen*, 1886, **233**, 11). This substance $C_{19}H_{20}O_3N_2$ has a mean molecular weight 209, forms bisphenylmethylpyrazolone with phenylhydrazine, and when warmed with hydrochloric acid or alcohol yields ethyl phenylcarbamate. It may be a mixture of ethyl phenylcarbamate and the substance derived from the hypothetical $C_8H_{10}O_2N_2$, containing 2Ph in the place of hydrogen: $2C_{19}H_{20}O_3N_2 = 2C_9H_{11}O_2N + C_8H_8Ph_2O_2N_2$. C. S.

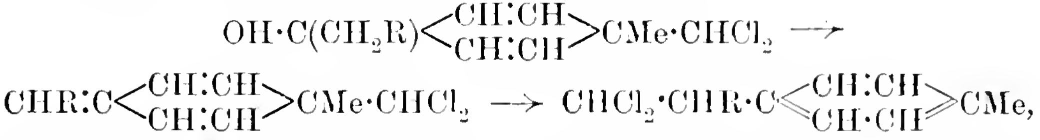
Chlorinated Alcohols [Phenols] of the Dihydrobenzene Series and their Transformation Products. KARL AUWERS (*Ber.*, 1906, **39**, 3718—3757. Compare Auwers and Keil, Abstr., 1903, i, 620; 1904, i, 26; Auwers and Hessenland, Abstr., 1905, i, 434).—The *product* $C_9H_{12}OCl_2$, obtained with magnesium methyl iodide by Grignard's reaction from 1-keto-2-methyl-2-dichloromethyl-1 : 2-dihydrobenzene, is an oil which boils at 112—114° under 9 mm. or at 121—122·5° under 13 mm. pressure, and has a sp. gr. 1·202 at 20°/4°, n_D 1·5023 at 19°, and a mol. refraction showing the presence of one double linking. The substance is extremely stable towards dehydrating agents, and is probably an oxide formed by intramolecular change from the tertiary alcohol constituting the product of the Grignard synthesis. When treated with concentrated sulphuric acid, it changes gradually into an *isomeride*, which forms stout crystals, melts at 40—41°, boils at 141—143° under 9 mm. pressure, and has a sp. gr. 1·2254 at 23·5°/4° or 1·2074 at 45°/4°, n_D 1·51419 at 46°, and a mol. refraction pointing to the presence of a ketone with one double linking; the coefficient of dispersion is slightly greater than for the oxide.

The *product*, $C_{10}H_{14}OCl_2$, formed with magnesium ethyl iodide by Grignard's synthesis from 1-keto-2-methyl-2-dichloromethyl-1 : 2-dihydrobenzene, is an oil, which boils at 130—131° under 9 mm. pressure, has a sp. gr. 1·1860 at 20°/4° or 1·1833 at 24°/4°, n_D 1·50251 at 20° or 1·50019 at 24°, resembles the methyl derivative in its stability towards dehydrating agents, and yields an oily *isomeride* on treatment with concentrated sulphuric acid.

All the preceding substances are more or less easily attacked by alkali hydroxides, being converted into chlorinated or non-chlorinated unsaturated acids, and finally into unsaturated hydrocarbons.

In the *para*-series, the derivatives of *as-o*-xylenol, *as-m*-xylenol, and *ψ*-cumenol behave in the same manner as the derivatives of the simpler *para*-substituted phenols.

The labile intermediate products of the series



$$OH\cdot C(CH_2R)<\begin{matrix}CH:CH\\CH:CH\end{matrix}>CMe\cdot CHCl_2 \longrightarrow$$

$$CHR:C<\begin{matrix}CH:CH\\CH:CH\end{matrix}>CMe\cdot CHCl_2 \longrightarrow CHCl_2\cdot CHR\cdot C\ll\begin{matrix}CH:CH\\CH\cdot CH\end{matrix}\gg CMe,$$

are *para*-derivatives of alkylidene 1 : 4-dihydrobenzenes and are isomeric with the final benzene derivatives; these substances, termed by the author "semibenzenes," have mol. refractions higher than the calculated, and abnormally high coefficients of dispersion as compared with the normal dispersions of the aromatic series.

The relation of these facts to the constitution of the semibenzenes is discussed. G. Y.

Phenyl Chlorothiocarbonates. HENRI RIVIER (*Bull. Soc. chim.*, 1906, [iii], **35**, 837—843).—*Phenyl chlorothioncarbonate*, $CSCl\cdot OPh$, obtained by the action of sodium phenoxide on thiocarbonyl chloride dissolved in chloroform, is a bright yellow liquid with a sharp odour, boils at 91° under 10 mm. and at 100° under 15 mm. pressure, crystallises at −0·5°, and has a sp. gr. 1·283 at 15°/4°. When dissolved in alcohol it decomposes, slowly in the cold, or immediately at 100°, forming *phenyl ethyl thioncarbonate*, OEt·CS·OPh. This is a colourless liquid, with a pleasant ethereal odour, has a sp. gr. 1·135 at 15°/4°, and boils at 124° under 12 mm. and at 130° under 17 mm. pressure. Sodium phenoxide converts phenyl chlorothioncarbonate into diphenyl thioncarbonate, and some of the latter is formed as a by-product in the primary reaction (compare Eckenroth and Kock, Abstr., 1894, i, 408). Phenyl chlorothioncarbonate reacts with thiophenol or, better, with the lead derivative of the latter to form *diphenyl dithiocarbonate*, SPh·CS·OPh, which forms golden-yellow prisms and melts at 51°. Ammonia solution in excess decomposes phenyl chlorothioncarbonate, forming phenol and ammonium thiocyanate and chloride, but with smaller quantities *phenyl thioncarbamate*, NH_2·CS·OPh, may be obtained. This separates from alcohol in flat, colourless needles and melts at 132—132·5°. With methylamine, *phenyl methylthioncarbamate*, NHMe·CS·OPh, is produced as an oil which could not be obtained pure. With aniline, *phenyl phenylthioncarbamate*, NHPh·CS·OPh, is obtained. This crystallises from alcohol in small, colourless needles and decomposes when heated, forming a liquid mixture of phenol and phenylthiocarbimide.

The author agrees with Orndorff and Richmond (Abstr., 1900, i, 156) that the substance described by Dixon (Trans., 1890, **57**, 268); Snape (Trans., 1896, **69**, 98), and Eckenroth and Kock (*loc. cit.*) as phenyl phenylthioncarbamate was probably thiocarbanilide. *Phenyl dimethylthioncarbamate*, NMe_2·CS·OPh, obtained by the action of dimethylamine on phenyl chlorothioncarbonate, separates from ether in colourless prisms and melts at 30—30·4°. *Phenyl phenylmethylthioncarbamate*, similarly obtained from methylaniline, forms colourless crystals and melts at 104°. Phenyl phenylethylthioncarbamate melts at 69·2° (compare Billeter and Strohl, Abstr., 1888, 364). The last three substances are less readily decomposed by alkalis, water, or alcohol than their analogues described above. T. A. H.

Preparation of 2-Nitro-6-amino-4-acetaminophenol. LEOPOLD CASSELLA & Co. (D.R.-P. 172978). When 4-acetaminophenol is strongly nitrated two nitro-groups are introduced into the ortho-positions with respect to the hydroxyl group. The dinitro-compound when converted into its sodium derivative and reduced by warming with dilute aqueous sodium sulphide, gives rise to *2-nitro-6-amino-4-acetaminophenol*, $NHAc·C_6H_2(NO_2)(NH_2)·OH$, which crystallises from alcohol in brownish-red needles and melts at 190°. This substance is feebly basic; its *hydrochloride*, which crystallises in yellow needles, being dissociated by water; with nitrous acid, it yields an orange-yellow *diazo*-derivative. G. T. M.

Preparation of Diaryl Sulphides. FERD. MAUTHNER (*Ber.*, 1906, **39**, 3593—3598. Compare this vol., i, 421; Bourgeois, Abstr., 1896, i, 17).—A number of diaryl sulphides, of which those described below are new, have been prepared by the action of aryl iodides on sodium arylmercaptides in presence of copper powder. This reaction constitutes a general method for the preparation of the diaryl sulphides.

o-*Tolyl*-m-*tolyl sulphide*, $C_{14}H_{14}S$, from *o*-thiocresol and *m*-iodotoluene, is a colourless, odourless oil, which boils at 170° under 11 mm. pressure. *Di*-m-*tolyl sulphide*, from *m*-thiocresol and *m*-iodotoluene, is a colourless oil which boils at 174° under 12 mm. pressure.

o-*Methoxydiphenyl sulphide*, $C_{13}H_{12}OS$, from thiophenol and *o*-iodoanisole, is a colourless oil which has an unpleasant, aromatic odour, and boils at 196° under 11 mm. pressure.

m-*Thioanisole*, C_7H_8OS, prepared by diazotisation of *m*-anisidine and treatment of the solution with potassium xanthate at 80—90°, boils at 224—225° (corr.). *Di*-m-*methoxyphenyl sulphide*, $C_{14}H_{14}O_2S$, is a colourless oil which boils at 214—215° under 10 mm. pressure.

As the iodonitrobenzenes are unstable, the corresponding bromides are employed in the preparation of nitro-derivatives of diphenyl sulphide.

o-*Nitrodiphenyl sulphide*, $C_{12}H_{11}O_2NS$, crystallises from light petroleum in long, yellow needles, melts at 77°, and gives a green coloration with concentrated sulphuric acid. On reduction with stannous chloride and hydrochloric acid, it yields o-*aminodiphenyl sulphide*, which is obtained as a colourless oil; the *sulphate*, $C_{12}H_{13}O_4NS_2$, forms long needles and is decomposed by water. The *acetyl* derivative, $C_{14}H_{13}ONS$, crystallises in colourless needles and melts at 86°.

o-*Nitrophenyl* o-*tolyl sulphide*, $C_{12}H_{11}O_2NS$, from *o*-thiocresol and *o*-bromonitrobenzene, crystallises from light petroleum in yellow needles and melts at 86—87°, and gives a green coloration with concentrated sulphuric acid. G. Y.

Aromatic Sulphine Bases. II. FRIEDRICH KEHRMANN and ALFRED DUTTENHÖFER (*Ber.*, 1906, **39**, 3559—3560. Compare this vol., i, 83).—Aryldimethylsulphine salts are formed by heating the aromatic mercaptans with an excess of methyl sulphate at 100°; the methyl mercaptide formed in the first stage of the reaction combines with methyl sulphate, forming the aryldimethylsulphine methyl sulphate, $SRMe_2 \cdot O \cdot SO_3Me$. The corresponding aryldiethylsulphine salts are formed in the same manner but less readily.

Phenyldimethylsulphine platinichloride, $(C_8H_{11}S)_2PtCl_6$, forms orange, yellow crystals, melts and decomposes at 165—166°, and is slightly soluble in water.

α-*Naphthyldimethylsulphine platinichloride*, $(C_{12}H_{13}S)_2PtCl_6$, is obtained as a sandy, crystalline, flesh-coloured precipitate, which melts and decomposes at 174°. β-*Naphthyldimethylsulphine platinichloride* forms a flesh-coloured, crystalline powder, and melts and decomposes at 177°. G. Y.

Preparation of Aminonaphthols. FRANZ SACHS (D.R.-P. 173522. Compare this vol., i, 829).—The sulphonic group of a naphtholsulphonic acid may be replaced with great facility by an amino-group when the acid is heated with sodamide at high temperatures, especially in the absence of air, or in the presence of inert diluting materials such as naphthalene or quinoline. β-Naphthol-7-sulphonic acid furnished 2-amino-β-naphthol, whilst α-naphthol-5-sulphonic acid gave rise to 5-amino-α-naphthol. These products were characterised by their dibenzoyl derivatives.

In some cases isomeric change occurred; thus β-naphthol-6-sulphonic acid gave a good yield of 5-amino-β-naphthol and β-naphthol-8-sulphonic acid furnished a mixture of 5-amino-β-naphthol and other isomerides. G. T. M.

Resolution of Aminobenzyl-β-naphthol into its Optical Antipodes.

Mario Betti (*Gazzetta*, 1906, **36**, ii, 392—394. Compare Abstr., 1901, i, 611).—Racemic aminobenzyl-β-naphthol (aminobenzylidene-β-naphthol) can be readily separated into its constituents by adding an alcoholic solution of tartaric acid to a solution of the compound in 95 per cent. alcohol; in the course of twelve hours, the liquid deposits the d-*amine*-d-*tartrate* in almost theoretical amount. This tartrate forms small, shining crystals and begins to soften and turn yellow at about 180° and decomposes above 240°.

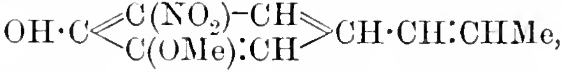
d-*Aminobenzyl-β-naphthol*, $NH_2\cdot CHPh\cdot C_{10}H_6\cdot OH$, crystallises from ether in white, silky needles, melts at 137°, and in benzene solution has $[\alpha]_D$ $+58{\cdot}84°$ at 18°. Its *hydrochloride* has $[\alpha]_D$ $+52{\cdot}89°$ in alcoholic solution at 18°.

l-*Aminobenzyl-β-naphthol* melts at 136—137°, and has $[\alpha]_D$ $-58{\cdot}96°$. Its *hydrochloride* has $[\alpha]_D$ $-52{\cdot}51°$.

It is noteworthy that the racemic compound melts at a lower temperature (124°) than its constituent isomerides, this being very seldom the case. T. H. P.

Nitro*iso*eugenol.

Ernesto Puxeddu and Matteo Comella (*Gazzetta*, 1906, **36**, ii, 450—455).—*Nitro*iso*eugenol*,



$$OH\cdot C\!<\!\begin{matrix}C(NO_2){-}CH\\C(OMe){:}CH\end{matrix}\!>\!CH\cdot CH{:}CHMe,$$

prepared by the action of nitric acid on *iso*eugenol in acetic acid solution, separates from amyl or *iso*butyl alcohol in a reddish-yellow, amorphous mass decomposing at about 150°, and is readily soluble in alcohol or chloroform; it dissolves in concentrated nitric acid, giving a reddish-brown coloration, and in concentrated sulphuric acid forming an intensely brown solution; it is very readily soluble in dilute alkali solution, yielding a blood-red liquid with a peculiar odour. Its *bromo*-derivative, $C_7H_7O_4N\cdot CBr{:}CHMe$ or $C_7H_7O_4N\cdot CH{:}CBrMe$, separates from alcohol as a reddish-yellow, amorphous powder, and begins to decompose at 175°; it dissolves in amyl alcohol, acetic acid, concentrated nitric or sulphuric acid or dilute alkali solution, and, to a slight extent, in ether or light petroleum. Its *acetyl* derivative, $C_{12}H_{13}O_5N$, is deposited from alcohol as a yellowish-brown, amorphous powder decomposing above 200°. T. H. P.

Preparation of a Di-*o*-phenetidinedisulphonic Acid.

Aktien Gesellschaft für Anilin-Fabrikation (D.R.-P. 174497. Compare this vol., i, 837).—*Di-*o*-phenetidinedisulphonic acid*,

$$C_{12}H_4(OEt)_2(NH_2)_2(SO_3H)_2\ [3:3':4:4':6:6'],$$

is readily produced by treating di-*o*-phenetidine with fuming sulphuric acid at moderately low temperatures; it is readily soluble in water, whereas its sodium salt dissolves only sparingly and crystallises from water in lustrous leaflets. G. T. M.

Preparation of 4-Alkyloxy-α-naphthols. BADISCHE ANILIN- UND SODA-FABRIK (D.R.-P. 173730).—Generally the two hydroxyl groups of the dihydroxynaphthalenes are alkylated with equal readiness, so that the dialkyloxynaphthalenes are produced, but it now found that 1 : 4-dihydroxynaphthalene readily undergoes monoalkylation when the etherification process is discontinued so soon as the dihydroxy-compound has disappeared.

4-Methoxy-α-naphthol, $OMe\cdot C_{10}H_6\cdot OH$, is prepared by dissolving 1 : 4-dihydroxynaphthalene in cold methyl-alcoholic hydrochloric acid and leaving the solution at the ordinary temperature for fifteen hours. When crystallised from light petroleum or benzene, the ether separates in colourless needles and melts at 131° (Abstr., 1900, i, 601).

4-Ethoxy-α-naphthol, produced by heating 1 : 4 dihydroxynaphthalene with alcoholic hydrochloric acid for thirty minutes, crystallises in colourless needles and melts at 104—105° (*loc. cit.*).

4-iso*Amyloxy-α-naphthol* forms colourless needles and melts at 98°.

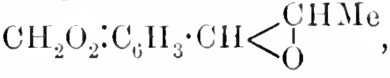
G. T. M.

Preparation of Anethole and *iso*Safrole Oxides. PAUL HÖRING (D.R.-P. 174496).—The dibromides of anethole and *iso*safrole when warmed with granulated marble in moist acetone solution are readily converted into their hydroxy-bromides,

$$OMe\cdot C_6H_4\cdot CH(OH)\cdot CHMeBr$$

and $CH_2O_2\!:\!C_6H_3\cdot CH(OH)\cdot CHMeBr$. These substances or their acetyl derivatives when warmed with alcoholic sodium hydroxide or ethoxide lose another molecule of hydrogen bromide and become transformed into the corresponding oxides.

Anethole oxide,  $OMe\cdot C_6H_4\cdot CH<\begin{matrix}CHMe\\ |\\ O\end{matrix}$, is an oil boiling at 132° under 11 mm. pressure and having a sp. gr. 1·0637 at 17°. When warmed at 190—210° under ordinary pressure, the oxide undergoes isomeric change into the *ketone,* $OMe\cdot C_6H_4\cdot CH_2\cdot COMe$, which boils at 267—269° under ordinary pressure and at 136—138° under 12 mm. pressure and has a sp. gr. 1·0707 at 17°.

iso*Safrole oxide,*  $CH_2O_2\!:\!C_6H_3\cdot CH<\begin{matrix}CHMe\\ |\\ O\end{matrix}$, is a colourless oil having a more pleasant odour than the preceding oxide; it boils at 149—151° under 12 mm. pressure and has a sp. gr. 1·2128 at 17°. At 200—220° this oxide is transformed with development of heat into the isomeric *ketone,* $CH_2O_2\!:\!C_6H_3\cdot CH_2\cdot COMe$; this boils at 149—151° under 11 mm. or at 283—284° under the ordinary pressure, and has the sp. gr. 1·2017 at 17°.

G. T. M.

Amount of Cholesterol in Fats and Mineral Oils and their Probable Genetic Relationships. M. A. RAKUSIN (*Chem. Zeit.*, 1906, **30**, 1041—1042).—The presence of cholesterol in a number of oils of animal, vegetable, and mineral origin has been shown both by means of the colour reactions described by Tschugaeff, which consist in heating the substance with acetyl chloride in the presence of zinc chloride or with trichloroacetic acid, and by measurement of the optical rotation. The presence of cholesterol in mineral oils is regarded as a clear proof of their origin from animal and vegetable sources; the low optical activity of some of the American oils is attributed to their containing the racemic modification of cholesterol.

P. H.

Colour Phenomena Connected with Liquid Crystals. [Cholesterol Compounds].

Otto Lehmann (*Chem. Centr.*, 1906, ii, 858; from *Physikal. Zeit.*, 7, 578—584).—An account of the play of colours observed when cholesteryl acetate propionate, *iso*butyrate, *n*-valerate, *iso*valerate, decoate, or octoate are examined between crossed nicols. When fused cholesteryl decoate is slowly cooled, it passes through two modifications of liquid crystals. In the first form the crystals are very small and mobile, and exhibit feeble double refraction; in the second form the crystals are larger and less mobile, but their double refraction is greater. The colour phenomena exhibited by mixtures of the decoate or the benzoate with *p*-azoxyphenetole are also described. P. H.

Solubility of Certain Benzoates in Water: Strontium Benzoate.

Raffaello Pajetta (*Gazzetta*, 1906, **36**, iii, 67—70).—The solubility of strontium benzoate is as follows in grams of anhydrous salt per 100 grams of solution: at 15·7°, 5·31; at 24·7°, 5·40; at 31·4°, 5·40; at 40·9°, 5·77. Of potassium benzoate (expressed similarly) at 17·5°, 41·1; at 25·0°, 42·4; at 33·3°, 44·0; at 50·0°, 46·6. Of normal lead benzoate, at 18°, 0·149; at 40·6°, 0·249; at 49·5°, 0·310. The solubility of zinc benzoate diminishes with rise of temperature: at 15·9°, 2·55; at 17·0°, 2·49; at 27·8°, 2·14; at 31·3°, 2·05; at 37·5°, 1·87; at 49·8°, 1·62; at 58·0°, 1·45. W. A. D.

Preparation of Benzoylalkylaminoethanols [Alkylaminoethyl Benzoates].

Chemische Fabrik auf Aktien vorm. E. Schering (D.R.-P. 175080).—By benzoylating the alkylaminoethanols or their salts, benzoyl derivatives are obtained which have valuable anæsthetic properties.

Diethylaminoethyl benzoate, $NEt_2\cdot CH_2\cdot CH_2\cdot OBz$, obtained by treating diethylaminoethanol with benzoic anhydride in aqueous solution is a viscid oil; its hydrochloride separates from a mixture of alcohol and ether in long needles melting at 124—125°. This salt is much more soluble in water than the hydrochlorides of the known synthetical local anæsthetics: "holocaine," "eucaine," &c., and is much less toxic than "stovaine" (dimethylaminodimethylethylcarbinyl benzoate hydrochloride).

Dimethylaminoethyl benzoate, $NMe_2\cdot CH_2\cdot CH_2\cdot OBz$, is a viscid oil; its *hydrochloride* readily dissolves in water or alcohol, but not in ether, crystallises in white leaflets, and melts at 136—137°.

Methylaminoethyl benzoate is an oil which forms a hydrochloride, crystallising in lustrous leaflets and melting at 108—109°.

Diisoamylaminoethyl benzoate crystallises from a mixture of ethyl acetate and light petroleum and melts at 87—88°; its *oxalate* crystallises from water in spherical aggregates of sparingly soluble needles and melts at 152—153°. G. T. M.

Reversible Reactions among Derivatives of Organic Acids. JOACHIM BIEHRINGER and WILHELM BORSUM (*Ber.*, 1906, 39, 3348—3356).—The qualitative conditions are discussed under which a number of simple organic reactions become reversible. Thus, in sealed tubes at 150°, benzoic acid and acetyl chloride form benzoyl chloride and acetic acid, but at 120°, under ordinary pressure, change proceeds in the contrary direction. Whereas the interaction of benzoic acid and acetamide takes place in one direction only, ethyl acetate and benzamide yield acetamide and ethyl benzoate when heated for six hours under pressure at 260°, whilst the reverse change takes place on heating under pressure from 270° to 290°. Phenyl benzoate and ammonia interact in sealed tubes at 150°, whilst benzamide and phenol yield phenyl benzoate when heated. Other cases considered are the interaction of oxalic acid and acetamide, of benzoic acid and acetanilide, and of acetanilide and benzoyl chloride. Diacetyl-*o*-tolidine and *o*-tolidine when heated together in sealed tubes at 240° give rise to *monoacetyl-o-tolidine*, forming pale yellow crystals which melt at 133—135°, rapidly become green when exposed to the atmosphere, and decompose when moist at 100°. E. F. A.

Formation and Behaviour of Thiobenzanilide. ROBERTO CIUSA (*Atti R. Accad. Lincei*, 1906, [v], 15, ii. 379—384).—The author has prepared thiobenzanilide by the action of phosphorus pentasulphide on benzophenoneoxime and, after crystallising from alcohol and light petroleum, dissolving in dilute potassium hydroxide solution and precipitating by means of carbon dioxide and again crystallising from light petroleum, it melted at 96°. When dissolved in potassium hydroxide solution and boiled with silver nitrate, it is converted into benzanilide.

With silver nitrate, thiobenzanilide forms a *salt*, $(C_{13}H_{11}NS)_2,AgNO_3$, which separates in long, yellow needles, deflagrates and melts at 115°, and is soluble in chloroform, ethyl acetate, or methyl alcohol.

When reduced by means of zinc dust and potassium hydroxide solution, thiobenzanilide gives a yellow oil, which yields benzaldehyde on boiling with hydrochloric acid. As the thioanilides are easily obtained, this reaction affords a ready means of passing from an acid to the corresponding aldehyde. T. H. P.

Preparation of Arylanthranilic Acids. IRMA GOLDBERG and FRITZ ULLMANN (D.R.-P. 173523).—Arylanthranilic acids are obtained when anthranilic acid is treated with aromatic bromo-derivatives in the presence of copper as a catalyst.

Phenylanthranilic acid is produced in a state of purity by heating to boiling a mixture of anthranilic acid, potassium carbonate, bromobenzene, and amyl alcohol to which a small amount of cuprous chloride has been added. The reaction takes place in accordance with the following equation: $NH_2{\cdot}C_6H_4{\cdot}CO_2H + PhBr + K_2CO_3 =$

$$NHPh{\cdot}C_6H_4{\cdot}CO_2K + KBr + CO_2 + H_2O.$$

By replacing bromobenzene by other brominated benzene derivatives, similar arylanthranilic acids are prepared; *p*-bromonitrobenzene gives rise to 4-*nitrophenylanthranilic acid*, $NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2H$, which crystallises in yellow needles and melts at 211°. The use of *p*-dibromobenzene leads to the formation of p-*phenylenebis*-o-*aminobenzoic acid*, $C_6H_4(NH\cdot C_6H_4\cdot CO_2H)_2$, which melts at 288°; it is very sparingly soluble in the ordinary organic media, but dissolves in boiling nitrobenzene. G. T. M.

Thiocyanates and Thiocarbimides. VI.

Treat B. Johnson (*J. Amer. Chem. Soc.*, 1906, **28**, 1454—1461. Compare Wheeler and Johnson, Abstr., 1902, i, 760).—Phenylthioacetic, *m*- and *p*-bromothiobenzoic, and *m*-nitrothiobenzoic acids have been prepared by dissolving the corresponding acyl chlorides in a solution of potassium hydrogen sulphide and treating the resulting potassium salts with hydrochloric or sulphuric acid. These thiol acids react smoothly with methyl, ethyl, and benzyl thiocyanates with formation of the corresponding dithiocarbamates. Phenylthioacetic, *p*-bromothiobenzoic, and *m*-nitrothiobenzoic acids react quantitatively with phenylthiocarbimide with production of the corresponding acylanilines.

[With Ernest Bateman, Erik S. Palmer, and Charles A. Brautlecht.]—*Phenylthioacetic acid*, $CH_2Ph\cdot CO\cdot SH$, is obtained as a limpid oil, and when left in the air is slowly converted into the disulphide. *Diphenylacetyl disulphide*, $(CH_2Ph\cdot CO)_2S_2$, prepared by suspending finely powdered iodine in an aqueous solution of sodium phenylthioacetate, crystallises from alcohol in transparent plates and melts at 62°. *Methyl phenylacetyldithiocarbamate*,

$$CH_2Ph\cdot CO\cdot NH\cdot CS\cdot SMe,$$

crystallises in slender prisms and melts at 133°. The corresponding *ethyl* ester separates from alcohol in lemon-yellow prisms and melts at 125°.

m-*Bromothiobenzoic acid*, $C_6H_4Br\cdot CO\cdot SH$, separates from light petroleum as a pale yellow, crystalline powder, melts at 58°, and is very soluble in alcohol, ether, or benzene. *Methyl*-m-*bromobenzoyldithiocarbamate*, $C_6H_4Br\cdot CO\cdot NH\cdot CS\cdot SMe$, crystallises in needles and melts at 124°; the corresponding *ethyl* and *benzyl* esters crystallise in prisms and melt at 131° and 113° respectively.

p-*Bromothiobenzoic acid*, $C_6H_4Br\cdot CO\cdot SH$, crystallises from hot alcohol in prisms and melts at 78—79°. *p*-Bromobenzoylaniline melts at 201—202° instead of at 197° as stated by Raveill (Abstr., 1884, 600). *Methyl* p-*bromobenzoyldithiocarbamate*, $C_6H_4Br\cdot CO\cdot NH\cdot CS\cdot SMe$, crystallises in needles and melts at 152°; the corresponding *ethyl* ester forms pale yellow needles and melts at 116°.

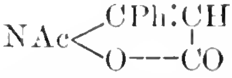
m-*Nitrothiobenzoic acid*, $NO_2\cdot C_6H_4\cdot CO\cdot SH$, forms light yellow, prismatic crystals and melts at 89—90°; the *sodium* salt is very soluble in water. *Methyl* m-*nitrobenzoyldithiocarbamate*,

$$NO_2\cdot C_6H_4\cdot CO\cdot NH\cdot CS\cdot SMe,$$

crystallises from benzene in yellow needles, melts at 162°, and is very soluble in benzene and sparingly so in alcohol; the corresponding *ethyl* ester separates from hot alcohol in yellow prisms and melts at 158°. E. G.

Unsaturated Compounds. II. The Addition of Free Hydroxylamine to Cinnamic Acid. Constitution and Derivatives of β-Hydroxylamino-β-phenylpropionic Acid. THEODOR POSNER (*Ber.*, 1906, **39**, 3515—3529. Compare Abstr., 1904, i, 160). —The substance produced by the direct addition of hydroxylamine to cinnamic acid was formerly regarded as being α-hydroxylamino-β-phenylpropionic acid, because on reduction it yielded the compound which was then considered to be α-aminodihydrocinnamic acid. The latter has since been shown to be β-amino-β-dihydrocinnamic acid (Abstr., 1905, i, 577), and consequently the original additive compound is *β-hydroxylamino-β-phenylpropionic acid*, $OH{\cdot}NH{\cdot}CHPh{\cdot}CH_2{\cdot}CO_2H$, melting at 166°. *Diacetyl* and *dibenzoyl-β-hydroxylamino-β-phenyl-propionic acids* form colourless crystals melting respectively at 166—167° and 110°.

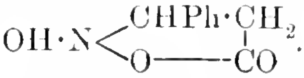
On oxidation with ammoniacal silver nitrate, the hydroxylamino-acid furnishes 3-phenyl*iso*oxazolone, the *nitroso*-derivative of which melts at 143°.

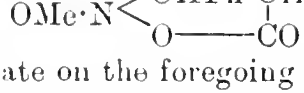
*Acetyl-3-phenyl*iso*oxazolone*,  $NAc<\begin{array}{l}CPh{:}CH\\ \quad\quad\quad\ |\\ O{-}{-}{-}CO\end{array}$, forms white needles melting at 137—138°; it is readily soluble in aqueous ammonia and alkalis, and is reprecipitated by dilute acids.

*Bromo-3-phenyl*iso*oxazolone*, $C_9H_6O_2NBr$, produced by brominating 3-phenyl*iso*oxazolone in chloroform solution, separates from methyl alcohol in prismatic crystals and melts at 121—122°. β-Hydroxylamino-β-phenylpropionic acid is very readily alkylated by treatment with a mixture of the appropriate alcohol and concentrated hydrochloric acid on the water-bath. *β-Methoxylamino-β-phenylpropionic acid* and the *ethoxyl* compound crystallise in colourless needles and melt respectively at 101·5—102·5° and 74·5—75°. Both alkyl derivatives are readily hydrolysed by alkalis, although fairly stable to cold dilute acids. They both furnish, on oxidation with ammoniacal silver nitrate, good yields of 3-phenyl*iso*oxazolone.

β-Nitrosohydroxylamino-β-phenylpropionic acid,

$$CHPh{\cdot}N(OH)(NO){\cdot}CH_2{\cdot}CO_2H,$$

is a very unstable compound obtained by the action of nitrous acid on β-hydroxylamino-β-phenylpropionic acid or its alkyl derivatives; when quickly prepared and isolated, it forms a colourless, crystalline powder melting at 133°. On heating or even on dissolving it in warm benzene, it evolves nitrous fumes and changes into *2-hydroxy-3-phenyl*iso*oxazolidone*,  $OH{\cdot}N<\begin{array}{l}CHPh{\cdot}CH_2\\ \quad\quad\quad\quad\ |\\ O{-}{-}{-}{-}{-}{-}CO\end{array}$, a pale yellow, crystalline powder easily soluble in methyl or ethyl alcohol, and dissolving readily in aqueous alkalis, but not in dilute acids.

*2-Methoxy-3-phenyl*iso*oxazolidone*,  $OMe{\cdot}N<\begin{array}{l}CHPh{\cdot}CH_2\\ \quad\quad\quad\quad\ |\\ O{-}{-}{-}{-}{-}{-}CO\end{array}$, is obtained either by the action of methyl sulphate on the foregoing compound, or by the decomposition in benzene solution of the nitroso-compound of β-methoxylamino-β-phenylpropionic acid; it crystallises from benzene in rectangular prisms and melts at 128°.

2-*Ethoxy-3-phenyl*iso*oxazolidone* melts at 109°, and, like the foregoing methyl compound, is insoluble in aqueous alkalis.

On attempting to acetylate 2-hydroxy-3-plenyl*iso*oxazolidone with acetic anhydride, a crystalline product was obtained which was decomposed by sodium carbonate into an acidic and a neutral part. The acidic compound has a composition approximating to $C_{18}H_{14}O_6$, the neutral substance corresponds with the formula $C_{22}H_{18}O_4$. G. T. M.

Condensation of Acetylenic Nitriles with Amines. General Method of Synthesis of β-Substituted Derivatives of β-Amino-substituted Acrylonitriles. Charles Moureu and I. Lazennec (*Compt. rend.*, 1906, **143**, 553—555. Compare this vol., i, 148, 240, 276, 432).—Phenylpropiolonitrile unites directly with piperidine to form *β-piperidyl-β-phenylacrylonitrile*, $C_5NH_{10}\cdot CPh\colon CH\cdot CN$, which is a neutral substance melting at 92°, stable towards alkalis, but readily hydrolysed by hydrochloric, picric, or oxalic acid with the regeneration of piperidine and formation of cyanoacetophenone, according to the equations: $C_5NH_{10}\cdot CPh\colon CH\cdot CN + H_2O = C_5NH_{11} +$

$$[OH\cdot CPh\colon CH\cdot CN] \longrightarrow COPh\cdot CH_2\cdot CN.$$

This reaction between acetylenic nitriles and primary or secondary amines is a general one, and the following compounds were thus prepared: *β-Benzylamino-β-amylacrylonitrile*,

$$CH_2Ph\cdot NH\cdot C(C_5H_{11})\colon CH\cdot CN,$$

melting at 64—65°; *β-piperidyl-β-amylacrylonitrile*,

$$C_5NH_{10}\cdot C(C_5H_{11})\colon CH\cdot CN,$$

boiling at 218—219° (corr.) under 23 mm. pressure, and having a sp. gr. 0·950 at 24°; *β-benzylamino-β-hexylacrylonitrile*,

$$CH_2Ph\cdot NH\cdot C(C_6H_{13})\colon CH\cdot CN,$$

melting at 48°; *β-piperidyl-β-hexylacrylonitrile*,

$$C_5NH_{10}\cdot C(C_6H_{13})\colon CH\cdot CN,$$

boiling at 236—238° (corr.) under 27 mm. pressure and having a sp. gr. 0·943 at 24°; *β-benzylamino-β-phenylacrylonitrile*,

$$CH_2Ph\cdot NH\cdot CPh\colon CH\cdot CN,$$

melting at 86°; *β-diethylamino-β-phenylacrylonitrile*, $NEt_2\cdot CPh\colon CH\cdot CN$, melting at 70°; and *β-piperidyl-β-phenylacrylonitrile*, melting at 92°.
M. A. W.

Condensation Products of Acetylenic Esters and Amines. Charles Moureu and I. Lazennec (*Compt. rend.*, 1906, **143**, 596—598. Compare preceding abstract).—The acetylenic esters readily condense with primary and secondary amines to form the amino-substituted derivative of the corresponding ethylene ester, and these compounds do not form salts with acids as stated by Ruhemann and Cunnington (Trans., 1899, **75**, 954), but are hydrolysed with regeneration of the base and formation of the corresponding β-ketonic ester. Thus, ethyl phenylpropiolate condenses with diethylamine to form ethyl β-diethylamino-β-phenylacrylate, $NEt_2\cdot CPh\colon CH\cdot CO_2Et$, which is readily hydrolysed in the cold by acids yielding the corresponding salt of diethylamine and ethyl benzoylacetate. The hydrolysis is effected by passing hydrogen chloride into an ethereal solution of the compound or by adding to the solution an equivalent quantity of picric or oxalic acid dissolved in ether and alcohol. The following compounds were obtained: *ethyl β-diethylamino-β-amylacrylate*,

$C_5H_{11}\cdot C(NEt_2)\colon CH\cdot CO_2Et$,

boiling at 170—178° under 26 mm. pressure and having a sp. gr. 0·9316 at 24°; *ethyl β-diethylamino-β-hexylacrylate*,

$C_6H_{13}\cdot C(NEt_2)\colon CH\cdot CO_2Et$,

boiling at 185—195° under 24 mm. pressure, and having a sp. gr. 0·9214 at 24°; *ethyl β-benzylamino-β-phenylacrylate*,

$CH_2Ph\cdot NH\cdot CPh\colon CH\cdot CO_2Et$,

melting at 72°; and *ethyl β-piperidyl-β-phenylacrylate*,

$C_5NH_{10}\cdot CPh\colon CH\cdot CO_2Et$,

boiling at 225—228° (corr.) under 23 mm. pressure, and having a sp. gr. 1·072 at 24°.

M. A. W.

Preparation of Hydroxyethyl Salicylate. Badische Anilin- und Soda-Fabrik (D.R.-P. 173776).—*β-Hydroxyethyl salicylate*, $OH\cdot C_6H_4\cdot CO_2\cdot CH_2\cdot CH_2\cdot OH$, the hitherto unknown monosalicylate of ethylene glycol, is readily prepared by the interaction of the metallic salicylates and the ethylene halogen hydrins; thus on heating at 140—150° for several hours a mixture of sodium salicylate and ethylene chlorohydrin, and extracting the product successively with water and ether, the ester is obtained as solid melting at 37°, and boiling at 169—170° under 12 mm. pressure. With ferric chloride it develops a violet coloration.

G. T. M.

Reductions with Phenylhydrazine. I. New Method of Preparing 5-Aminosalicylic Acid. Ernesto Puxeddu (*Gazzetta*, 1906, **36**, ii, 87—89. Compare Abstr., 1905, i, 842).—5-Aminosalicylic acid, $[CO_2H : OH : NH_2 = 1 : 2 : 5]$, is easily prepared by warming 5-nitrosalicylic acid with phenylhydrazine; action begins at slightly above 100° and proceeds rapidly. The yield is good.

W. A. D.

Constitution of the Aromatic Purpuric Acids. IX. Behaviour on Oxidation with Potassium Hypobromite. Walther Borsche and G. Gahrtz (*Ber.*, 1906, **39**, 3359—3366. Compare Abstr., 1905, i, 894).—Potassium *m*-purpurate when oxidised with potassium hypobromite yields 2 : 6-dinitro-3-hydroxybenzonitrile of which the *aniline* derivative crystallises in golden-yellow needles melting at 162—163°, and the *acetate* forms yellow, glistening platelets melting at 122—123°. Potassium *o*-tolylpurpurate under similar treatment yields 2 : 6-dinitro-3-hydroxy-4-toluonitrile. 4-*Bromo*-2 : 6-*dinitro-3-hydroxybenzonitrile*, obtained on oxidising potassium bromo-*m*-purpurate, crystallises in yellow needles melting at 152°, the *aniline* salt forms canary-yellow needles melting at 185°, whilst 4-*bromo*-2 : 6-*dinitro-3-hydroxybenzamide* separates from water in glistening, yellowish-white plates melting at 231°. Potassium naphthylpurpurate gives rise to 2 : 4-*dinitro*-1-*hydroxy-3-naphthonitrile*, crystallising in bright yellow, glistening needles which melt at 165—166°: the *aniline* salt is a yellow, crystalline powder melting at 152°.

Cyanopicric acid (2 : 4 : 6-*trinitro-3-hydroxybenzonitrile*), prepared by nitration of dinitrohydroxybenzonitrile, crystallises in yellowish-white needles or plates and melts at 131—132°: the *aniline* salt forms yellow needles which melt at 179—180°. E. F. A.

Conversion of Racemic Compounds into Optically Active Compounds. WILLY MARCKWALD and DAVID M. PAUL (*Ber.*, 1906, **39**, 3654—3655. Compare Abstr., 1905, i, 285).—When *l*-mandelic acid is heated with an equivalent quantity of brucine for twenty hours at 150—160° and the acid recovered, it is found to be dextrorotatory with $[\alpha]_D$ +0·45° to +0·6°. When *r*-mandelic acid is heated with other alkaloids, the recovered acid is found to be dextrorotatory, but the amount of rotation varies with the alkaloid employed. With strychnine the recovered acid has $[\alpha]_D$ +2·05° and with nicotine +0·4°.

r-*p*-Methoxymandelic acid has $[\alpha]_D$ +1·2° to +1·5°, when heated with brucine or strychnine, and β-phenyllactic acid has $[\alpha]_D$ −0·16° when heated with brucine for five hours at 150—160°.

α-Methylbutyric acid, and β-phenyl-α-methylpropionic acid are not affected when heated with strychnine, neither is α-methoxyphenylacetic acid when heated with brucine, whereas with strychnine it has $[\alpha]_D$ +0·32°. J. J. S.

Di-*p*-methylbenzilic Acid (*pp′*-Tolilic Acid). ERWIN GISIGER (*Ber.*, 1906, **39**, 3589. Compare Gattermann, this vol., i, 589).—Di-*p*-methylbenzilic acid is prepared by boiling di-*p*-methylbenzoin with 20 per cent. potassium hydroxide solution through which a current of air is passed; it melts at 135° and gives a blood-red coloration with concentrated sulphuric acid. The *barium* salt, $(C_{16}H_{15}O_3)_2Ba$, forms white leaflets; the *methyl* ester, $C_{17}H_{18}O_3$, crystallises from alcohol in needles and melts at 82°; the *acetyl* derivative, $C_{18}H_{18}O_4$, separates from light petroleum in small crystals, melts at 92°, and is readily hydrolysed. G. Y.

Influence of the Position of the Ethylene Linking on the Electro-affinity and Characters of Unsaturated Alicyclic Acids. GINO ABATI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1906, [iii], **12**, 220—226).—From a study of the affinity constants of the naphthoic and the hydronaphthoic acids, benzoic acid, phthalic and the hydrophthalic acids, it is seen that, apart from the strongly negative character of the aromatic nucleus, the presence and position of the double linking have no small influence on the energy of an acid. In the αα- and βγ-positions, the double linking produces a great increase in the value of the electrical conductivity, whilst when it is in the αβ- or γδ-position, the values of the conductivity are not much greater than those of the corresponding saturated acids.

The explanation given by Fichter and Pfister (Abstr., 1904, i, 965) of their results on the basis of Thiele's theory of partial valencies is fallacious. According to Thiele's theory, the γδ-, &c., acids should be as unsaturated as the βγ acids, whilst the fact is that they are far weaker than these and have constants not differing greatly from those of the αβ-acids. This contradiction of Thiele's theory is confirmed by the constants for acids having a double linking in the αα-position with respect to the two carboxyl groups. For instance, in the case of the four tetrahydrophthalic acids, the Δ^1 acid should, according to Thiele's theory, be the most saturated and should hence be the least energetic. Instead, however, the constant of this acid is the greatest of the four and is five times that of the Δ^4-acid, which has six partial valencies. Similar disagreement with this theory is offered by the constants for citraconic, mesaconic, and itaconic acids.

When treated with alkali hydroxides, unsaturated $\beta\gamma$-acids do not pass completely into the $\alpha\beta$-isomerides, the reaction being reversible. Further, in the reduction of phthalic acid by means of sodium amalgam, there is a marked tendency to the formation of acids with a double linking in the $\beta\gamma$-position, although the temperature is kept at about 150° for some three hours and the proportion of sodium hydroxide present in the liquid ultimately reaches 15 or 20 per cent. It is therefore unsafe to assign the $\beta\gamma$-constitution to acids on the sole ground that they undergo transformation with alkali hydroxides, as has been done by Perkin and Pickles in the case of the tetrahydro*iso*phthalic acids (Trans., 1905, **87**, 293). T. H. P.

Hydrophthalic Acids: Affinity Constants of Two New Anhydrides. II. GINO ABATI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1906, [iii], **12**, 207—210. Compare Abstr., 1905, i, 599).—Conductivity measurements of solutions of the two new hydrophthalic anhydrides (*loc. cit.*) lead to the following values: (1) For $\Delta^{1:3}$-dihydrophthalic anhydride, $\mu_\infty = 377$ and $K = 0.0798$. (2) For *cis*-Δ^3-tetrahydrophthalic anhydride, $\mu_\infty = 376$ and $K = 0.0581$.

Titration of aqueous solutions of the anhydrides with barium hydroxide solution, using methyl-orange as indicator, shows that, although they cannot be obtained in the solid state in the form of acids, they behave as acids when dissolved in water; this fact is also shown by the high value of the affinity constants, which are in accord with the constitutions given previously (*loc. cit.*), as it has been repeatedly observed that a double bond in the $\beta\gamma$-position effects a marked increase in the energy of unsaturated acids. T. H. P.

Hydrophthalic Acids: Transformation by Heat of the New Dihydrophthalic Anhydrides. Characters of the *p*-Methoxyphenylhydrophthalimides. III. GINO ABATI and ANDREA CONTALDI (*Rend. Accad. Sci. Fis. Mat., Napoli*, 1906, [iii], **12**, 211—219. Compare preceding abstract).—When heated at about 225° for some two hours, $\Delta^{1:3}$-dihydrophthalic anhydride (compare Abati and de Bernardinis, Abstr., 1905, i, 599) is converted into another anhydride, which is possibly the $\Delta^{2:5}$-compound regarded by von Baeyer (Abstr., 1892, 1211) as incapable of existence. When its alcoholic solution is treated with *p*-anisidine, it yields p-*methoxyphenyldihydrophthalimide*, which forms white needles melting at 98°, and as it does not correspond with any of the derivatives obtained from the known dihydrophthalic anhydrides, must be regarded as the $\Delta^{2:5}$-compound. Hence, when the $\Delta^{1:3}$-anhydride is heated, the double linking in the $\alpha\alpha$-position migrates to the neighbouring $\alpha\beta$-position, whilst the other double linking retains its place in the $\beta\gamma$-position.

p-*Methoxyphenyl*-$\Delta^{1:3}$-*dihydrophthalimide* forms yellow crystals melting at 101°.

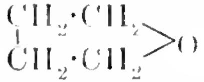
A table is given showing the melting points of the dihydrophthalic and tetrahydrophthalic anhydrides, and the melting points and colours of the *p*-methoxyphenylimides formed from these anhydrides. In general, the anhydrides exhibiting similar physical and chemical characters yield imides similar to one another.

Halochromism is exhibited by all the dihydrophthalimides when dissolved in sulphuric acid, whilst of the tetrahydrophthalimides only the Δ^1- and Δ^3-compounds show this phenomenon, a fact which illustrates the influence of the position of the ethylene linking with respect to the phenyldiketopyrrolidine grouping. T. H. P.

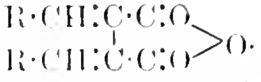
β-Benzylideneglutaric Acid. HERMANN A. MÜLLER (*Ber.*, 1906, **39**, 3590—3591. Compare Fittig and Roedel, Abstr., 1895, i, 141; Fittig, Abstr., 1898, i, 11; Fichter and Bauer, Abstr., *ibid.*, 662; Thiele and Meisenheimer, Abstr., 1899, i, 603).—The condensation of benzaldehyde with ethyl tricarballylate in ethereal solution in presence of sodium ethoxide leads to the formation of *β-benzylideneglutaric anhydride*,  $CHPh{:}C{<}{\begin{matrix}CH_2\cdot CO\\CH_2\cdot CO\end{matrix}}{>}O$, which crystallises in colourless, strongly refracting leaflets or long, flat prisms, melts at 44—45°, is volatile in a current of steam, and with alkali hydroxides forms *salts* of β-benzylideneglutaric acid; the *acid* is unstable and yields the anhydride immediately on liberation. *β-Benzylideneglutaranil*, $C_{18}H_{15}O_2N$, formed by heating the anhydride with aniline, crystallises in glistening leaflets and melts at 90°. When boiled with aqueous sodium hydroxide, β-benzylideneglutaric acid yields two *acids*, melting at 184° and 145° respectively. G. Y.

Colour of Fulgides and of other Unsaturated Compounds. HANS STOBBE (*Annalen*, 1906, **349**, 333—371).—The author cites numerous examples to show that the colour of the fulgenic acids and of similarly constituted substances is to be explained not only by the number and the position of the chromophoric phenyl and carboxyl groups in the carbon chain, but also by the influence of the conjugated double linkings. The fact that α : δ-diphenyl-$\Delta^{\alpha\gamma}$-butadiene-δ-carboxylic acid and α : δ-diphenylfulgenic acid are colourless, whereas α : δ-diphenyl-$\Delta^{\alpha\gamma}$-butadiene-γ-carboxylic acid is yellow, is accounted for on stereochemical grounds.

The more pronounced colour of the fulgides is not due to heterocyclic ring formation; examples are quoted to show that such formation results in a diminution or disappearance of the colour. The selective absorption of the fulgides can be brought into harmony with the "quinone" theory, inasmuch as these compounds are ortho- and paraquinonoid derivatives of tetrahydrofurfuran,



$$\begin{matrix}CH_2\cdot CH_2\\ | \\ CH_2\cdot CH_2\end{matrix}{>}O$$



$$\begin{matrix}R\cdot CH{:}C\cdot C{:}O\\ | \\ R\cdot CH{:}C\cdot C{:}O\end{matrix}{>}O.$$

In chemical and physical properties they resemble Thiele's fulvenes (Abstr., 1900, i, 298) and "quinonoid" hydrocarbons (Abstr., 1904, i, 491).

The absorption spectra of certain fulgides have been measured in $N/32$ chloroform solution.

Tetramethylfulgide absorbs only in the ultra violet; the presence of each phenyl group increases by 58μ. the length of the absorption band in the visible spectrum. C. S.

Condensation Products of Gallic Acid with Formaldehyde and Carbamide, or with Formaldehyde and Urethanes. ARNOLD VOSWINKEL (D.R.-P. 171788).—Carbamide (1 mol.) condenses with gallic acid (2 mols.) and formaldehyde, giving rise to a methylene-carbamido-gallic acid having the composition $C_{17}H_{16}O_{11}N_2$. The condensation occurs in dilute alcohol in the presence of mineral acids, and the product is a pale grey powder which melts and decomposes at 210° and has an intensely bitter taste. The compound forms an insoluble basic bismuth salt. G. T. M.

Cetraric Acid. OSCAR SIMON (*Arch. Pharm.*, 1906, **244**, 459—466. Compare Abstr., 1903, i, 98).—The products obtained by treating cetraric acid with aqueous sodium hydroxide and zinc powder have been examined further. From the crude mixture of phenols, 3 : 5-dihydroxy-1 : 2-dimethylbenzene, $C_8H_{10}O_2$ (Abstr., 1904, i, 406), has been isolated. When treated with bromine (4 mols.) in chloroform solution, it yields crystalline *dibromo-* and *tribromo-*derivatives; these melt at 98 and 112° respectively, and are converted into the ketobromide, $C_8H_6O_2Br_4$, when treated with excess of bromine in acetic acid solution.

From the same source yellow crystals were obtained which melt at 119—121°, contain C 63·4, H 5·5, and have molecular weight 164 (determined cryoscopically in naphthalene); this *substance* does not contain methoxyl; it is soluble in alkali hydroxides and carbonates and gives a green coloration with ferric chloride; when it is treated in the cold with aniline in alcoholic solution, it yields an orange-yellow *anilide*, which melts and decomposes at 189—190°, and contains C 73·4, H 6·1, N 7·0; and with excess of bromine in acetic acid solution it forms a *bromide* which melts at 116—121°, contains C 17·5, H 1·8, Br 76·6, and is insoluble in aqueous sodium carbonate.

From the resinous mass obtained when the product of the action of aqueous sodium hydroxide and zinc powder is poured into dilute sulphuric acid, a yellow, crystalline *substance* has been obtained which melts at 129—132°, contains C 65·5, H 6·1 ($C_{10}H_{12}O_3$?), and has molecular weight 180 (determined cryoscopically in naphthalene); this substance, when treated in alcoholic solution with aniline, forms a red *anilide*, $C_{16}H_{17}O_2N$, which melts and decomposes at 184°, and when treated with a large excess of bromine in acetic acid solution, it yields the ketobromide, $C_8H_6O_2Br_4$.

When cetraric acid, $C_{20}H_{18}O_9$, is treated with bromine, either directly or in acetic acid or chloroform solution, it yields a *bromo-*derivative, probably a mixture of $C_{20}H_{16}O_9Br_2$ and $C_{19}H_{16}O_7Br_2$, which melts at 181—185°, still contains methoxyl, and dissolves slowly in aqueous sodium carbonate. C. F. B.

Behaviour of Benzaldehyde in Presence of Iodoxybenzene and under the Action of Light. Luigi Mascarelli (*Atti R. Accad. Lincei*, 1906, [v], **15**, ii, 375—379).—The interaction of benzaldehyde and iodoxybenzene under the influence of light yields: (1) Benzoic acid, by the reaction, $2Ph·CHO + PhIO_2 = 2Ph·CO_2H + PhI$. (2) A *trimeric benzaldehyde*, $(C_7H_6O)_3$, which separates from acetic acid in stable, white crystals melting at 250°. (3) Stilbene, which may be formed either by the reduction of benzaldehyde by iodosobenzene formed as an intermediate product in the oxidation of benzaldehyde to benzoic acid by the iodoxybenzene: $2Ph·CHO + 2Ph·OI = CHPh:CHPh + 2Ph·IO_2$; or by the decomposition of a complex oily product, $CHPh:I·Ph$ or $Ph·I(CHPh)_2$, which could not be obtained pure, and yields stilbene and iodobenzene on distillation. T. H. P.

Additive Products Formed by Trinitrobenzene with Aromatic Substances containing the Side-chain ·CH:N·. Roberto Ciusa (*Gazzetta*, 1906, **36**, ii, 94—98).—Benzaldehydephenylhydrazone combines with trinitrobenzene in warm alcoholic solution to form the *additive* compound $CHPh:N_2HPh,C_6H_3(NO_2)_3$, which forms dark red crystals and melts at 134°; the analogous *trinitrotoluene* derivative, $CHPh:N_2HPh,C_6H_2Me(NO_2)_3$, forms dark red needles and melts at 84°. *Benzaldehydephenylhydrazone picrate*, $CHPh:N_2HPh,C_7H_3O_7N_3$, prepared similarly by using picric acid, forms blackish-violet needles with a metallic reflex, and melts at 117°. m-*Nitrobenzaldehydephenylhydrazone picrate*, $NO_2·C_6H_4·CH:N_2HPh,C_6H_3O_7N_3$, crystallises in chestnut coloured needles with a violet sheen and melts at 118°.

Benzylideneazine combines with trinitrotoluene in alcoholic solution, giving yellow needles of the *additive* compound,

$$CHPh:N·N:CHPh,C_6H_2Me(NO_2)_3,$$

which melts at 97—98°. *Benzylideneazine picrate*, $C_{14}H_{12}N_2,C_6H_3O_7N_3$, forms small, canary-yellow needles and melts at 148°. *Furfuralazine picrate*, $(C_4H_3O·CH:)_2N_2,C_6H_3O_7N_3$, crystallises from alcohol in greenish-yellow needles, darkens at 155°, and melts and decomposes at 157°. Benzylideneaniline picrate, $CHPh:NPh,C_6H_3O_7N_3$, crystallises in golden-yellow needles and melts at 183°. *Salicylideneaniline picrate*, $OH·C_6H_4·CH:NPh,C_6H_3O_7N_3$, forms lustrous, yellow needles and melts at 153—154°. *Cinnamylideneaniline*, $CHPh:CH·CH:NPh,C_6H_3O_7N_3$, crystallises in orange-yellow needles or plates and melts at 139°.

W. A. D.

Some Aromatic Aldehydes and Ketones. Karl Auwers (*Ber.*, 1906, **39**, 3757—3764. Compare Auwers and Hessenland, Abstr., 1905, i, 434).—*p*-Methylhydrocinnamaldehyde (von Miller and Rohde, Abstr., 1890, 978) is a colourless oil which boils at 220—230° under atmospheric pressure, has a sp. gr. 0·9928 at 18·5°/18·5°, and forms a *semicarbazone*, $C_{11}H_{15}ON_3$, crystallising in long, flat, glistening needles and melting at 170—171°. p-*Ethylbenzoylmethyl chloride*, $C_6H_4Et·CO·CH_2Cl$, prepared by Friedel and Craft's synthesis from ethylbenzene and chloroacetyl chloride, crystallises from light petroleum in white scales, melts at 38—39°, boils at 145—148° under 8 mm. pressure, and forms a *semicarbazone*, $C_{11}H_{14}ON_3Cl$, crystallising in slender, white needles and melting at 153—154°. p-*Ethylbenzoylmethyl acetate*, $C_6H_4Et\cdot CO\cdot CH_2\cdot OAc$, prepared by boiling the chloride with potassium acetate and glacial acetic acid, crystallises in white prisms, melts at 61—62°, and when boiled with alcoholic sodium hydroxide yields the *carbinol*, $C_6H_4Et\cdot CO\cdot CH_2\cdot OH$. This crystallises in yellow leaflets, melts at 67—68°, and has a sweet flavour; the *semicarbazone*, $C_{11}H_{15}O_2N_3$, crystallises in white scales and melts at 161°. p-*Ethylphenylacetaldehyde*, $C_6H_4Et\cdot CH_2\cdot CHO$, prepared by reducing the ketonic alcohol with sodium amalgam in aqueous alcoholic carbonate solution through which a current of carbon dioxide is passed, and treatment of the resulting glycol with concentrated sulphuric acid, is obtained as an oil; this has an odour of cuminaldehyde, and forms a *semicarbazone*, $C_{11}H_{15}ON_3$, crystallising in slender, white needles and melting at 162—164°.

p-Methylbenzoylmethyl chloride melts at 57—58° (compare Kunckell, Abstr., 1897, i, 282; Collet, Abstr., 1898, i, 139; Ryan, *ibid.*, 649); the acetate melts at 85—86° (83—83·5°, Collet, 1898, i, 123). p-*Methylbenzoylcarbinol*, $C_6H_4Me\cdot CO\cdot CH_2\cdot OH$, crystallises in light yellow prisms, melts at 89—89·5°, and forms a *semicarbazone*, $C_{10}H_{13}O_2N_3$, crystallising in white needles and melting at 165°. Reduction of the ketonic alcohol with sodium amalgam and treatment of the *product* with concentrated sulphuric acid leads to the formation of only a small amount of an *oil*, which has a characteristic odour of elderberries, and forms a *semicarbazone*, $C_{10}H_{13}ON_3$, melting at 208°. A small amount of the same semicarbazone, but melting at 212—213°, is obtained from the product formed on boiling *p*-methyl-*ββ*-dichloroethyl benzene with aqueous potassium hydroxide.

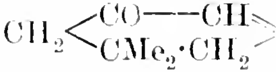
α-Chloro-p-*methylhydratropic acid*, $C_6H_4Me\cdot CClMe\cdot CO_2H$, prepared by the action of hydrogen cyanide on *p*-methylacetophenone (compare Janssen, Abstr., 1889, 596) and treatment of the product with concentrated hydrochloric acid at 130° (Spiegel, Abstr., 1881, 277), crystallises from carbon disulphide and melts at 116—118°.

p-*Methylhydratropaldehyde*, $C_6H_4Me\cdot CHMe\cdot COH$, prepared by the action of ethyl chloroacetate and sodamide on *p*-methylacetophenone (compare Claisen, Abstr., 1905, i, 287), boils at 227—228° under atmospheric pressure, and is identical with the aldehyde obtained from cymene by Etard's reaction; it forms a semicarbazone crystallising in slender, white needles melting at 155—157°.

The supposed aldehyde-semicarbazone previously obtained (Abstr., 1905, i, 434) from dichloro-*p*-cumic acid is now found to be the semicarbazone of *p*-tolylacetone; it is accompanied by a small amount of a *semicarbazone* of an aldehyde which remains in the mother liquors on recrystallisation.

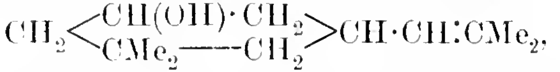
5-*Ethylsalicylaldehyde*, $OH\cdot C_6H_3Et\cdot COH$, prepared from *p*-ethylphenol by Reimer's synthesis, is an oil; the *semicarbazone*, $C_{10}H_{13}O_2N_3$, crystallises in nacreous leaflets and melts at 208°. G. Y.

Synthesis of a Ketone Isomeric with Xylitone. EMIL KNOEVENAGEL and RUDOLF SCHWARTZ (*Ber.*, 1906, 39, 3441—3451. Compare Kerp and Müller, Abstr., 1898, i, 265; Pinner, Abstr., 1882, 941).—A compound isomeric with Pinner's xylitone may be synthesised by the action of sodium ethoxide on a mixture of ethyl acetoacetate and acetophenone; it is represented as iso*butenyldimethyl*cyclo*hexenone*,



$CH_2<\substack{CO\text{——}CH\\ CMe_2\cdot CH_2}>C\cdot CH\colon CMe_2$,

and distils at 132—134° under 12 mm. pressure, or at 246° under atmospheric pressure. It is not readily volatile with steam, and has a sp. gr. 0·9365 at 19°/4°. The molecular refraction is higher even than what would be required for the enolic compound. It yields a *tetrabromide*, which is extremely unstable, a *phenylhydrazone* melting at 80—81°, an *oxime*, $C_{12}H_{19}ON$, melting at various temperatures between 85° and 108°, and a *semicarbazone* melting at 167—168°. When reduced with sodium and alcohol, it yields iso*butenyldimethyl*cyclo*hexanol*,



$$CH_2<\substack{CH(OH)\cdot CH_2\\ CMe_2\text{——}CH_2}>CH\cdot CH\colon CMe_2,$$

which boils at 122—123° under 12 mm. pressure, and has a sp. gr. 0·8886 at 23·5°/4° and n_D 1·4675 at 23·5°. The *dibromide* is unstable, and the *acetate* distils at 244—247°. When oxidised with chromic acid mixture, the alcohol yields the corresponding ketone iso*butenyldimethyl*cyclo*hexanone*, $C_{12}H_{20}O$, which boils at 109—110° under 12 mm. pressure. It has a sp. gr. 0·8823 at 19·5°/4° and n_D 1·1397 at 19·5°. With phosphoric oxide, the alcohol yields iso*butenyldimethyl*cyclo*hexene*,

$CH_2<\substack{CH\text{==}CH\\ CMe_2\cdot CH_2}>CH\cdot CH\colon CMe_2$,

boiling at 195—196°. It has a sp. gr. 0·8246 at 23°/4° and n_D 1·4653.

iso*Butenyldimethyl*cyclo*hexenylamine*,

$$CH_2<\substack{C(NH_2)\colon CH\\ CMe_2\text{—}CH_2}>CH\cdot CH\colon CMe_2,$$

obtained by reducing the oxime, boils at 108—112° under 14 mm. pressure. A by-product is an oil boiling at 150—160° under 10 mm. pressure. The base is unstable, decomposing slowly with formation of ammonia. The *sulphate*, $C_{12}H_{21}N,H_2SO_4$, melts at 115—116°, and the *phenylthiocarbamide* at 129—130°. J. J. S.

Condensation Products of High Molecular Weight from Acetone. Alkaline Condensation of Acetone. EMIL KNOEVENAGEL and LEO BLACH (*Ber.*, 1906, 39, 3451—3457).—*iso*Butenyldimethyl-*cyclo*hexenone (compare preceding abstract) yields acetone and *iso*-acetophorone when boiled with concentrated formic acid. Two products, isomeric with *iso*butenyldimethyl*cyclo*hexenone, have been prepared from the higher fractions obtained by the action of sodium ethoxide on acetone. The first, α-iso*xylitone* is identical with Kerp and Müller's xylitone. It boils at 117—119° under 11 mm. pressure, has a sp. gr. 0·9396 at 16°/4° and n_D 1·5249 at 16°; it yields an oily oxime, and a semicarbazone which melts at about 159°. The second compound, β-iso*xylitone*, distils at 129—131·5° under 11 mm. pressure, has a sp. gr. 0·9513 at 18°/4°, n_D 1·5182 at 18°, and yields a *semicarbazone* melting at 175°. J. J. S.

Condensation Products of High Molecular Weight from Acetone. Acid Condensation of Acetone. EMIL KNOEVENAGEL and HANS BEER (*Ber.*, 1906, 39, 3457—3466. Compare preceding abstracts).—The following fractions have been isolated from the products of high boiling point obtained by the condensation of acetone with hydrochloric acid: 120—122°, 127—129°, 137—139°, and 141—144°, all under a pressure of 11 mm. The first fraction has the composition $C_{15}H_{24}O_2$ and yields a semicarbazone which melts at 118°. The fraction 127—129° appears to be identical with Pinner's xylitone (Abstr., 1882, 911). With semicarbazide it yields a derivative melting at 151°, and oily products with hydroxylamine or phenylhydrazine. It is not identical with synthetical xylitone or with α- and *β-iso*xylitones. The analytical data of fractions three and four agree with the formula $C_{19}H_{26}O$.

From a second specimen of Kahlbaum's high boiling products, two fractions, 128—130° and 140—142°, were obtained. The first fraction, after removal of small amounts of oxygenated compound by means of sodium hydrogen sulphite, gave analytical data agreeing with the formula $C_{15}H_{24}$. It has a sp. gr. 0·9062 at 16·1° and n_D 1·5338, and may probably be a sesquiterpene. The second fraction gives analytical results agreeing with either $C_{18}H_{30}$ or $C_{21}H_{36}$. J. J. S.

Nitro- and Amino-propiophenones. Ezio Comanducci and Luigi Pescitelli (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1906, [iii], **12**, 286—291).—By the action of fuming nitric acid on propiophenone under various conditions, the authors have obtained the three nitropropiophenones.

o-*Nitropropiophenone* (?), $NO_2\cdot C_6H_4\cdot COEt$, crystallises from alcohol in yellow needles melting at 85°, and is soluble in water, ether, chloroform, or benzene.

m-Nitropropiophenone (?) (compare Barry, Abstr., 1874, 74) crystallises from alcohol in pale, yellow needles melting at 98°, dissolves in water, benzene, ether, chloroform, or light petroleum, and yields a white, crystalline product with sodium hydrogen sulphite.

p-*Nitropropiophenone* (?) separates from ether in yellowish-white crystals melting at 114°, dissolves rapidly in alcohol, chloroform, benzene, or alkali solution and to a less extent in water or light petroleum, and forms a white, crystalline compound with sodium hydrogen sulphite.

The aminopropiophenones obtained by reducing the *o* and *p*-nitro-compounds are white, and dissolve in water, alcohol, or ether, whilst that from the *m*-derivative is a syrup with an odour of strawberries and is soluble in water or alcohol; all of them give the alkaloid reactions. The *hydrochloride* of the *m*-amino derivative decomposes at 170° and melts at a slightly higher temperature, whilst those of the ortho- and para-compounds decompose without melting at about 200°. (Compare Kunckell, Abstr., 1900, i, 664.) T. H. P.

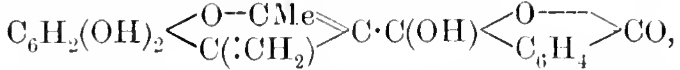
Migration of the Phenyl Group; Mode of Fixation of Hypoiodous Acid and the Elimination of Hydrogen Iodide. Marc Tiffeneau (*Compt. rend.*, 1906, **143**, 649—651. Compare Abstr., 1902, i, 666; 1904, i, 63; this vol., i, 662, 724).—Hydrocarbons of the general formula RAr C:CHR′ (where R and R′ represent alkyl groups which may be identical or different or replaced by hydrogen, and Ar represents an aryl group) form iodohydrins, which, on treatment with silver nitrate, are converted into the ketones, $R\cdot CO\cdot CHArR'$. Thus, *α-phenyl-Δ^{α}-*iso*amylene*, $CHPh{:}CHPr^{\beta}$, boiling at 204—206°, yields *α-phenyl*iso*valeraldehyde*, $CHPhPr^{\beta}\cdot CHO$, boiling at 222—223°. *β-Phenyl-Δ^{α}-amylene*, $CH_2{:}CPhPr^{\alpha}$, boiling at 198—200°, and having a sp. gr. 0·9138 at 0°, yields benzyl propyl ketone, $CH_2Ph\cdot COPr^{\alpha}$ (Blaise, Abstr., 1902, i, 164), which boils at 237—239°, has a sp. gr. 0·9889 at 0°, and forms a semicarbazone melting at 189°. *β-Phenyl-Δ^{β}-butylene*, $CPhMe{:}CHMe$, yields benzyl methyl ketone which has a sp. gr. 0·997 at 0° (Darzens, this vol., i, 63). *β-Phenyl-Δ^{β}-amylene*, $CPhMe{:}CHEt$, boiling at 199—201°, yields *α-phenylpropyl methyl ketone*, $CHPhEt\cdot COMe$, which boils at 225—227°, has a sp. gr. 0·979 at 0°, and forms a *semicarbazone* melting at 188°.

The iodohydrin of α-phenyl-Δ^{α}-*iso*butylene, $CHPh{:}CMe_2$, when treated with silver nitrate, yields a mixture of phenyl*iso*butaldehyde (Abstr., 1902, i, 666), and *phenylbutylene oxide*,  $O<\substack{CHPh\\|\\CMe_2}$, which boils at 213—215°; it is probable that in the case of this hydrocarbon the two iodohydrins, $CHPhI\cdot CMe_2\cdot OH$ and $OH\cdot CH\cdot Ph\cdot CIMe_2$, are formed, which, on elimination of hydrogen iodide, yield the corresponding ethylene oxide and unstable vinyl alcohol respectively, the latter changing into the isomeric aldehyde. M. A. W.

[*p*-Dimethylaminobenzylideneacetone.] Correction. FRANZ SACHS and WILLY LEWIN (*Ber.*, 1906, **39**, 3785).—*p*-Dimethylaminobenzylideneacetone sinters at 130° and melts at 134—135° and not at 230° and 234—235° as given previously (Abstr., 1903, i, 37. Compare Rupe and Siebel, this vol., i, 859). G. Y.

Combination of Phthalylacetylacetone with Pyrogallol.

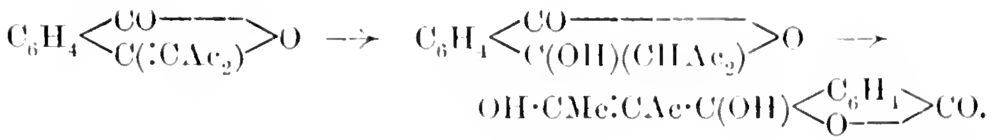
CARL BÜLOW and MAX DESENISS (*Ber.*, 1906, **39**, 3664—3667. Compare Abstr., 1901, i, 475; 1902, i, 554; 1905, i, 149, 294, 529; this vol., i, 588).—The *lactone* of *7 : 8-dihydroxy-2-methyl-4-methylene-1 : 4-benzopyranol-3-phthalylaldehydic acid*,



$$C_6H_2(OH)_2<\substack{O—CMe\\C({:}CH_2)}>C\cdot C(OH)<\substack{O——\\C_6H_4}>CO,$$

is obtained in the form of its hydrochloride by passing hydrogen chloride into an acetic acid solution of pyrogallol and phthalylacetylacetone and keeping the mixture at 0°. The *hydrochloride*, $C_{19}H_{14}O_6,HCl,1\cdot5H_2O$, crystallises from alcohol containing hydrogen chloride in red prisms, which decompose at about 109°. It dissolves in acetone, alcohol, benzene, or glacial acetic acid, but is insoluble in ether, and is readily hydrolysed by water. The *picrate*, $C_{25}H_{17}O_{13}N_3$, forms red crystals decomposing at 195—200°, and soluble in water and most organic solvents.

It is suggested that in the above condensation the phthalylacetylacetone forms an additive compound with water, and this then passes into the enolic form,



$$C_6H_4<\begin{matrix}CO\text{———}\\C(:CAc_2)\end{matrix}>O \longrightarrow C_6H_4<\begin{matrix}CO\text{—————}\\C(OH)(CHAc_2)\end{matrix}>O \longrightarrow$$
$$OH\cdot CMe:CAc\cdot C(OH)<\begin{matrix}C_6H_4\\O\text{——}\end{matrix}>CO.$$

J. J. S.

Sodium Hyposulphite as a Reducing Agent. II. Eugène Grandmougin (*Ber.*, 1906, **39**, 3561—3564. Compare this vol., i, 716).—In many reductions the use of sodium hyposulphite is to be preferred to that of the usual reducing agents, as in the preparation of β-naphthaquinone from Orange II. (Grandmougin and Michel, Abstr., 1892, 861), or of 1 : 4 diaminonaphthalene from 4-benzeneazo-1-naphthylamine (Bamberger and Schieffelin, Abstr., 1889, 495).

Sodium hyposulphite may be used in the reduction of compounds other than those containing an azo-group. Nitrobenzene gives poor yields of aniline; *o*-nitrophenol is reduced to *o*-aminophenol; in these cases sodium sulphide is a better reducing agent than the hyposulphite. The quinones: benzoquinone, β-naphthaquinone, and phenanthraquinone, are readily reduced by sodium hyposulphite to the corresponding quinols; oxanthranol is obtained more readily by reduction of anthraquinone in this manner than by Graebe and Liebermann's method (this Journal, 1872, **25**, 139).

Benzil is reduced by sodium hyposulphite to benzoin. G. Y.

Oxidation of Diaminophenols. Friedrich Kehrmann and H. Prager (*Ber.*, 1906, **39**, 3437—3441).—When a solution containing 2 : 4-diaminophenol hydrochloride and ferric chloride is mixed with sodium dichromate solution, greenish-black, glistening crystals of *aminobenzoquinoneimide dichromate*, $2NH:C_6H_3(NH_2):O,H_2Cr_2O_7$, are deposited. They dissolve to a certain extent in cold water, yielding a red solution and are completely decomposed by hot water. The *picrate*, $C_{12}H_9O_8N_5$, forms chocolate-brown crystals.

Corresponding salts of benzoquinoneimides have been obtained from 2 : 4-diamino-*o*-cresol; the *nitrate*, $NH:C_6H_2Me(NH_2):O,HNO_3$, is readily obtained on the addition of solid sodium nitrate to a mixture of diaminocresol hydrochloride and ferric chloride. It dissolves in water or alcohol, yielding solutions with a bluish-red colour. The *dichromate* and *picrate* have also been prepared.

The *nitrate* of *amino*-m-*methylbenzoquinoneimide* forms blackish-red needles readily soluble in water; the *dichromate* is readily soluble; the *mercurichloride* is sparingly soluble, and crystallises in blackish-red needles.

Corresponding reddish-violet salts have been obtained from diaminothymol. J. J. S.

1 : 4-Anthraquinone. C. Haslinger (*Ber.*, 1906, **39**, 3537—3538. Compare Dienel, this vol., i, 290).—The melting point of 1 : 4-anthraquinone formerly given as 206° must be regarded as a decomposition point, owing to the darkening of the substance which occurs even at 190°. The successive stages of the process of converting 1 : 4-anthraquinone into quinizarin take place very readily, the diacetylquinizarin being hydrolysed by cold concentrated acid instead of alcoholic potash as formerly described. G. T. M.

Preparation of Alkylated Aryl-*p*-diaminoanthraquinonesulphonic Acid. FARBWERKE VORM. MEISTER, LUCIUS, and BRÜNING (D.R.-P. 171131).—It has been found that the alkyl sulphates behave both as alkylating and sulphonating agents towards the aryldiaminoanthraquinones, so that alkylated aryl-*p*-diaminoanthraquinonesulphonic acids are obtained in one operation.

1-Amino-4-*p*-toluidinoanthraquinone is in this way converted into the colouring matter 4-p-*toluidino-4-dimethylaminoanthraquinonesulphonic acid* and 1 : 5-diamino-4 : 8-di-*p*-toluidinoanthraquinone furnishes 4 : 8-di-*p*-toluidino-1 : 5-tetramethyldiaminoanthraquinonesulphonic acid which is isolated in the form of its sodium salt. G. T. M.

Derivatives of the Aminoalizarins. GUSTAV SCHULTZ and J. ERBER (*J. pr. Chem.*, 1906, [ii], **74**, 275—296. Compare Abstr., 1902, i, 299).—The *α*-diacetylaminoalizarin melting at 205° crystallises from alcohol in glistening, golden-yellow needles, decomposes when sublimed, forming acetic acid and a red sublimate of *α*-aminoalizarin.

α-Dibenzoylaminoalizarin melts above 310°, and gives a red coloration with concentrated sulphuric acid.

β-Dibenzoylaminoalizarin gives a dark violet coloration with, but does not dissolve in, aqueous sodium hydroxide, becoming yellow again on addition of hydrochloric acid, and is then soluble in cold sodium hydroxide, forming a bluish-violet solution. With concentrated sulphuric acid it gives a red coloration, and after five minutes on addition of water yields *benzoyl-β-aminoalizarin*, $C_{21}H_{13}O_5N$, which crystallises from nitrobenzene in small, matted, dark green needles, melts at 275°, sublimes with partial decomposition forming yellow needles, is not hydrolysed by boiling concentrated hydrochloric acid, and gives with concentrated sulphuric acid a red, with aqueous sodium hydroxide a blue, coloration.

Prolonged action of concentrated sulphuric acid on the *β*-dibenzoylamino-derivative leads to the formation of a *product* which crystallises from nitrobenzene in yellowish-brown needles, melts at 320°, and closely resembles the monobenzoyl derivative.

α-Diazoalizarin sulphate (compare Brasch, Abstr., 1891, 1077) is formed by the action of sodium nitrite on *α*-aminoalizarin in ice-cooled, concentrated sulphuric acid solution; it separates on moderate dilution with alcohol in glistening, yellowish-brown needles, decomposes at about 140°, dissolves in much alcohol forming a brownish-violet solution becoming orange-yellow when heated, and when treated with aqueous alkali hydroxides at the ordinary temperature forms a reddish-violet solution which evolves nitrogen and becomes blue, the diazo-sulphate being converted into alizarin. When sublimed or boiled with dilute acids it yielded purpurin (Farbwerke vorm. Meister, Lucius, and Brüning, D.R.-P. 97688). The *α*-diazo-hydroxide is obtained as a brown, insoluble residue on treatment of the diazo-sulphate with water.

Diazotisation of β-aminoalizarin leads to the formation of the β-diazo-sulphate, which separates to a small extent in yellow crystals. On addition of water or alcohol to the acid solution, the β-diazo-hydroxide, $C_{14}H_5O_2(OH)_2{\cdot}N_2{\cdot}OH$, is thrown down as a scarlet or orange-red precipitate; this darkens on exposure to air, decomposes at 135°, and detonates when heated. It is decomposed by boiling dilute acids, aqueous alkali hydroxides, or alcohol, forming alizarin, only after prolonged drying or contact with dilute sulphuric acid.

With potassium iodide the diazo derivatives of alizarin form iodo-alizarins which dye mordanted stuffs brown. Azo-dyes cannot be obtained by coupling α-diazo-alizarin sulphate in alkaline or acid solution, whilst only a small amount of an unstable *dye* is formed by coupling β-diazoalizarin hydroxide with R-salt in alkaline solution.

Experiments are quoted to show that the stability of the diazo-derivatives of benzene and naphthalene increases with the size of the nucleus; it was to be expected, as is found, that the diazo-derivatives of anthracene would be still more stable. β-Diazoalizarin hydroxide resembles to some extent the diazonaphthalenes; in the α-derivatives the characteristics of the diazo-compounds are still less prominent.

When heated with sulphuric acid containing 20—40 per cent. of the anhydride, and poured into water, α-aminoalizarin yields a reddish-brown precipitate which, when boiled with water, is converted into *α-aminoalizarin-3 sulphonic acid* (*4-amino-1 : 2-dihydroxyanthraquinone-3-sulphonic acid*), $C_{14}H_4O_2(OH)_2(NH_2){\cdot}SO_3H$ (D.R.-P. 82938); this crystallises from alcohol in microscopic, nodular aggregates, is almost insoluble in ether, and forms a dark violet, insoluble *barium* salt, and a *silver* salt crystallising in microscopic, reddish-brown needles. Oxidation of the sulphonic acid leads to the formation of phthalic acid. When diazotised and heated in concentrated acid solution at 50—60°, α-aminoalizarin-3-sulphonic acid yields *purpurin-3-sulphonic acid*, which is isolated in the form of its sparingly soluble *potassium* salt, $C_{14}H_7O_8SK$, and is probably identical with the acid obtained by sulphonation of purpurin or by oxidation of alizarinsulphonic acid with nitric acid (D.R.-P. 84774), together with alizarin-3-sulphonic acid, which is considered to be identical with the acid formed by the action of fuming sulphuric acid on alizarin.

Purpurin-3-sulphonic and alizarin-3-sulphonic acids are formed also by boiling diazotised 4-aminoalizarin-3-sulphonic acid with aqueous sodium hydroxide. G. Y.

Preparation of a Base, $C_{10}H_{17}ON$, from Pulegone. FRIEDRICH W. SEMMLER (D.R.-P. 173775).—*α-Anhydropulegonehydroxylamine*, $C_{10}H_{17}ON$, produced by warming pulegonehydroxylamine with concentrated hydrochloric acid at 100°, when purified by means of its picrate, boils at 91° under 8 mm. pressure. The new base readily takes up four hydrogen atoms, and the resulting tetrahydro-base, $C_{10}H_{21}OK$, gives a characteristic thiocarbamide melting at 132°.

Benzylidene-α-anhydropulegonehydroxylamine, $CHPh{:}C_{10}H_{15}ON$, obtained by condensing the α-anhydro base with benzaldehyde in the presence of sodium ethoxide, crystallises from ether in needles melting at 105—106°; its picrate melts at 125—126°.

By the action of hydriodic acid on pulegonehydroxylamine, reduction and dehydration occur simultaneously, and a new base is obtained having the composition $C_{10}H_{19}ON$. G. T. M.

Chlorohydrochlorides of Pinene and Firpene.

GEORGE B. FRANKFORTER and FRANCIS C. FRARY (*J. Amer. Chem. Soc.*, 1906, **28**, 1461—1467).—The pinene used in these experiments was prepared from ordinary turpentine by distilling with steam, drying, and redistilling until it boiled constantly at 156—157°; it had a sp. gr. 0·8647 at 20°, n_D 1·46336 at 20°, and $[\alpha]_D$ +14·34°. The firpene was obtained from the western fir by distilling the crude pitch with steam and redistilling the terpene several times; the product had the composition $C_{10}H_{16}$, and differed from pinene in both chemical and physical properties. It boiled at 153—153·5° and had a sp. gr. 0·8598 at 20°, n_D 1·47299 at 20°, and $[\alpha]_D$ −47·2°. A method is described for the preparation of the hydrochlorides of these terpenes.

Pentachloropinene hydrochloride, $C_{10}H_{11}Cl_5,HCl$, obtained by treating a chloroform solution of pinene hydrochloride with potassium permanganate and hydrochloric acid, forms deliquescent, isometric crystals and melts at 173—174°. An attempt to prepare the compound from pinene itself instead of the hydrochloride was unsuccessful.

Nonachloropinene hydrochloride, $C_{10}H_7Cl_9,HCl$, obtained by the action of chlorine in bright sunlight on a solution in carbon tetrachloride of an uncrystallisable substance formed in the preparation of pentachloropinene hydrochloride, crystallises from alcohol, melts at 263—264° (uncorr.) and is very soluble in ether, benzene, chloroform, or carbon tetrachloride.

Firpene *hydrochloride*, $C_{10}H_{16},HCl$, melts at 130—131°, and is more volatile than pinene hydrochloride and more soluble in most of the ordinary solvents.

Dichlorofirpene hydrochloride, $C_{10}H_{14}Cl_2,HCl$, is less volatile and less soluble in alcohol than firpene hydrochloride.

Firpene *hydrobromide*, $C_{10}H_{16},HBr$, forms feathery crystals and melts at 102°.

By the action of nitrosyl chloride on firpene an oily, uncrystallisable substance is produced. E. G.

Dihydropinenesulphinic Acid, Dihydropinenecarbithionic Acid, Thioborneol, and Thiocamphor.

JOSEF HOUBEN and HANS DOESCHER (*Ber.*, 1906, **39**, 3503—3509. Compare Borsche and Lange, this vol., i, 679).—*Sodium dihydropinenesulphinate*,

$$C_{10}H_{17}\cdot SO_2Na,11(\text{or }12)H_2O,$$

prepared by passing sulphur dioxide into an ethereal solution of the magnesium compound of pinene hydrochloride and subsequently neutralising the portion soluble in ether with sodium carbonate, crystallises from water in well-defined, white leaflets having a faint characteristic odour.

Dihydropinenesulphinic acid, when set free by sulphuric acid from the foregoing salt, separates as a colourless oil slowly solidifying to needles on cooling in ice-water; it melts at 64° and probably is hydrated. When heated under 12 mm. pressure, it decomposes, yielding small quantities of camphane, and a similar change occurs on distilling it in steam.

Dihydropinenecarbithionic acid, obtained by adding carbon disulphide to the ethereal solution of the magnesium compound of pinene hydrochloride, is a brown oil having a camphoraceous odour; it is extremely decomposable, but yields characteristic metallic salts.

The interaction of sulphur and the magnesium compound of pinene hydrochloride leads to the production of thioborneol together with smaller quantities of dihydrodicamphene, bornyl disulphide, and other substances containing a larger proportion of sulphur.

On oxidation with dilute chromic acid at moderate temperatures, thioborneol is converted almost quantitatively into bornyl disulphide; at higher temperatures the latter decomposes into thioborneol and thiocamphor, so that by working under these conditions all the sulphur compounds obtained from the magnesium compound of pinene hydrochloride can be converted into thiocamphor. On exposure to the air or more rapidly by the action of oxygen, thiocamphor evolves sulphur dioxide and becomes converted into a colourless, odourless substance melting at 168°, which is probably bornyl sulphide. G. T. M.

Pitch [Oleo-resin] and Terpenes of the Norway Pine and the Douglas Fir. GEORGE B. FRANKFORTER (*J. Amer. Chem. Soc.*, 1906, **28**, 1467—1472).—The wood of the Norway pine (*Pinus resinosa*) yields from 6·2 to 42·6 per cent. of "pitch" [oleo-resin], which is obtained as a colourless, mobile liquid, has a sp. gr. 0·8137, n_D 1·47869, $[\alpha]_D$ +4°, and consists of about 22·1 per cent. of oil of turpentine, 77·3 per cent. of colophony, and 0·6 per cent. of water. The terpene obtained from this oleo-resin by steam distillation boils at 153—154°, has a sp. gr. 0·8636, n_D 1·47127, and $[\alpha]_D$ +17·39°. The terpene obtained by the process of destructive distillation boils at 158—160°, has a sp. gr. 0·8666, n_D 1·4716, and $[\alpha]_D$ −7·56°.

The wood of the Douglas fir (*Pseudotsuga taxifolia*) contains from 11·6 to 42·4 per cent. of oleo-resin which when first obtained is a clear, colourless liquid, but when left in the air becomes viscous and coloured. This product has a peculiar, aromatic odour, a sp. gr. 0·9821, n 1·51745, and $[\alpha]_D$ −8·82°, and contains about 22 per cent. of turpentine. The terpene obtained from this oleo-resin by steam distillation boils at 153·5—154°, has a sp. gr. 0·8621, n_D 1·47299, and $[\alpha]_D$ −47·2°. The terpene obtained by destructive distillation boils at 157—160°, has a sp. gr. 0·8662, n_D 1·47246, and $[\alpha]_D$ −29·4°. All the physical constants were determined at 20°. E. G.

Volatile Oil of Juniperus Phoenicea. J. RODIÉ (*Bull. Soc. chim.*, 1906, [iii], **35**, 922—925. Compare Umney and Bennett, *Pharm. J.*, **75**, 827).—The oil is bright yellowish-green and has an odour recalling those of juniper and savin, more especially the former. It is soluble in four to five times its volume of alcohol (90°), has a sp. gr. from 0·867—0·868 and its rotation in a 100 mm. tube varies from 2°54″ to 4°10′. The yield is from 0·45 to 0·5 per cent. of the plant.

The oil contains 92·3 per cent. of terpenes, principally pinene with traces of phellandrene and camphene and possibly dipentene, and 6·51 per cent. of other constituents boiling above 180°. T. A. H.

Oil of Myrrh. Kurt Lewinsohn (*Arch. Pharm.*, 1906, **244**, 412—435. Compare Tschirch and Bergmann, this vol., i, 197).—Three samples of commercial oil were examined, and one that was freshly prepared in the laboratory by distilling heerabol-myrrh with steam without addition of alkali. Three samples, including the fresh one, contained cuminaldehyde up to 1 per cent.; all samples contained small quantities of eugenol and *m*-cresol, and of acetic and palmitic acids, the latter being present as esters in the fresh sample, in the free state in the commercial samples. When one commercial sample, freed from these constituents, was mixed with light petroleum, a resin separated in amount equal to about 30 per cent. of the oil; this contained oxygen, and, when reduced in amyl alcoholic solution with sodium, yielded a sesquiterpene apparently identical with cadinene. By fractional distillation of the oils over metallic sodium, pinene, dipentene, and limonene were isolated; it is an open question whether the dipentene is present in the original oils.

From one commercial sample, a fourth *terpene*, $C_{10}H_{16}$, also was isolated, possibly an intermediate stage between limonene and dipentene; it boils at 78—80° under 20 mm. pressure, has a sp. gr. 0·847 at 20°, and $[\alpha]_D$ +80° at 20°; it forms a *tetrabromide* melting at 115°, a *monohydrochloride* melting at 6°, and an oily *nitrosochloride*. Two other, possibly new, *sesquiterpenes*, $C_{15}H_{24}$, were isolated also from the other two commercial samples; one, forming 24 per cent. of the oil from which it was obtained, boiled at 151—154° under 15 mm. pressure and had a sp. gr. 0·911 at 21°; the other boiled at 163—168° under 12 mm. pressure, and had sp. gr. 0·926 at 20° and $[\alpha]_D$ +22·75° at 20°. C. F. B.

Preparation of Normal Esters from Santal Oil. Knoll & Co. (D.R.-P. 173240).—The disadvantages attending the therapeutic application of santal oil and its known derivatives are overcome by converting the oil into an alkyl carbonate or an ester of an aromatic monobasic acid.

The *benzoyl* derivative of santal oil prepared either by heating the oil with benzoic anhydride at 110° or by condensing it with benzoic chloride in the presence of pyridine, has a sp. gr. 1·047 at 15°, and boils at 236—238° under 15 mm. pressure. This preparation is not volatile in steam and may thus be separated from the unbenzoylated santal oil.

The *salicyl* derivative is made by heating santal oil or pure santalol with salol and a small proportion of sodium hydroxide under diminished pressure until the elimination of phenol is complete; the sp. gr. is 1·07, and the salicylsantalol boils with partial decomposition at 250—260° under 20 mm. pressure.

Santalyl ethyl carbonate, prepared by condensing santal oil with ethyl chlorocarbonate in pyridine, boils at 180—185° under 25 mm. pressure, and has a sp. gr. 1·010 at 15°. The interaction of carbonyl chloride and santal oil under these conditions gives rise to the normal santalyl carbonate. G. T. M.

Baptisia Glucosides. K. Gorter (*Arch. Pharm.*, 1906, **244**, 401—405. Compare Abstr., 1898, i, 39).—ψ-Baptisin has now been isolated from the roots of *Baptisia tinctoria.*

ψ-Baptigenin melts at 303—304°. Its *sodium* derivative has the composition $C_{15}H_{11}O_6Na,H_2O$; when it is heated at 150° with ethyl iodide and a little alcohol, it is converted partially into a new *substance* which melts at 169°, contains C 71·3, H 4·9 per cent. ($C_{12}H_{10}O_3$?), dissolves readily in hot alcohol, and gives no coloration with ferric chloride in acetone solution. C. F. B.

Attempts to Prepare Aloe-emodin. Otto A. Oesterle (*Chem. Centr.*, 1906, ii, 882; from *Schweiz. Woch. Pharm.*, **44**, 509—512).—Aloetic acid was reduced by means of a very large excess of 33 per cent. potassium hydrogen sulphide to hydroaloetic acid; the latter compound when diazotised and heated with alcohol gave a small quantity of aloe-emodin. *Hydroaloetic acid* is a bluish-black, amorphous powder, which is insoluble in cold water, slightly soluble in hot water or alcohol, and dissolves readily to a deep blue solution in alkali hydroxides or carbonates; it is readily soluble in concentrated sulphuric acid, forming a brownish-yellow solution which, on addition of water, yields the unchanged acid and not a sulphate. P. H.

Elaterin. Jacques Pollak (*Ber.*, 1906, **39**, 3380—3382. Compare Thoms, *Chem. Zeit.*, 1906, 923; Berg, this vol., i, 596).—The analytical data for elaterin agree equally well with Zwenger's formula, $C_{20}H_{28}O_5$, or with that of Berg, $C_{28}H_{38}O_7$. The values obtained for the molecular weight vary considerably. The compound dissolves in alcoholic potash, but is partially decomposed and acetic acid is liberated. The amount of acetic acid produced on hydrolysing with dilute sulphuric acid (11·2 per cent. of acetyl) agrees best with Zwenger's formula.

J. J. S.

Elaterin. Franz von Hemmelmayr (*Ber.*, 1906, **39**, 3652—3653. Compare preceding abstract).—The analytical results obtained for elaterin and its bromo-derivative agree best with the formula $C_{21}H_{34}O_6$.

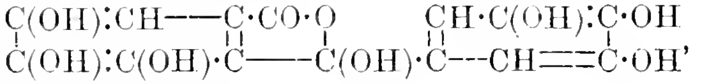
Elaterin yields a *di-phenylhydrazone*, and when heated with alcoholic sulphuric acid yields acetic acid and a phenol, *elateridin*, $C_{22}H_{32}O_5$. Boiling with potassium hydroxide solution converts elaterin into *elateric acid.* J. J. S.

Chlorophyll Absorption. M. Tsvett (*Chem. Centr.*, 1906, ii, 892—893; from *Ber. Deutsch. bot. Ges.*, 1906, **24**, 316—323).—A detailed account of the selective extraction of the various colouring matters in plants by a number of different solvents, together with a description of the method of separating these colouring matters.

P. H.

Kamala and Rottlerin. Hans Telle (*Arch. Pharm.*, 1906, **244**, 441—458. Compare A. G. Perkin, Trans., 1893, **63**, 975; 1895, **67**, 230).—Rottlerin, obtained from a commercial specimen of kamala, melted at 203—204°; the empirical formula $C_{11}H_{10}O_3$ (= 190) and the molecular weight 486 (determined cryoscopically in naphthalene) were confirmed. When heated for ten minutes with aqueous barium hydroxide solution, saturated in the cold, rottlerin yields 10 to 15 per cent. of phloroglucinol methyl ether, and also resinous substances, whilst some of it is converted into a reddish- or violet-brown isomeride, *ψ-rottlerin*, melting at 235°. When heated for some ten hours with zinc powder and 15 per cent. aqueous sodium hydroxide, rottlerin yields about 60 per cent. of resin and about 30 per cent. of phenols; also a considerable quantity of β-phenylpropionic acid, a little acetic acid, and a small quantity of a crystalline acid which melts at 185—185·5° and contains C 72·4, H 6·4 per cent. From the mixture of phenols, phloroglucinol mono- and di-methyl ethers were isolated. Probably phloroglucinol trimethyl ether was present also, and it was isolated with certainty from a product obtained by using 2 per cent., instead of 15 per cent., aqueous sodium hydroxide; from this product a small quantity of a *substance* melting at 170—172° and smelling like camphor was isolated. C. F. B.

Contitutional Formula of Tannin. Correction. J. Dekker (*Ber.*, 1906, 39, 3784. Compare this vol., i, 686).—The constitutional formula for tannin must be



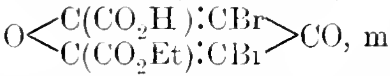
$$\begin{array}{l} \mathrm{C(OH){:}CH{-\!-}C{\cdot}CO{\cdot}O \qquad CH{\cdot}C(OH){:}C{\cdot}OH} \\ \mathrm{C(OH){:}C(OH){\cdot}C{-\!-}C(OH){\cdot}C{-}{-}{-}CH{=\!=}C{\cdot}OH} \end{array}$$

and not as previously given. G. Y.

Preparation of Bismuth Tannate. Chemische Fabrik von Heyden (D.R.-P. 172933).—When bismuth hydroxide is heated with a solution of tannin the well known bismuth subtannate,

$$Bi(OH)_2{\cdot}O{\cdot}C_{14}H_9O_8,$$

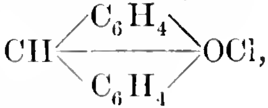
is produced; when, however, the interaction is effected at the ordinary temperature the *bismuth ditannate*, $Bi(OH)(O{\cdot}C_{14}H_9O_8)_2$, is obtained. This substance is prepared by adding a solution of bismuth nitrate in dilute nitric acid to a solution of tannin in aqueous sodium carbonate and stirring the mixture for six hours. The product is a pale yellow powder. On boiling with water, the ditannate loses tannic acid and is converted into the monotannate. G. T. M.

Brominated 4-Pyrones and their Hydroperbromides. Franz Feist) *Ber.*, 1906, 39, 3659—3664. Compare Collie and Tickle, Trans., 1900, 77, 1115; Feist and Baum, Abstr., 1905, i, 914; Hantzsch and Denstorff, this vol., i, 745).—*Ethyl hydrogen dibromochelidonate*,  $O{<}\begin{matrix} C(CO_2H){:}CBr \\ C(CO_2Et){:}CBr \end{matrix}{>}CO$, may be obtained from the mother liquors in the preparation of ethyl dibromochelidonate; it crystallises with $2H_2O$ and then melts at 85°, but in the anhydrous state melts at 182—183°.

Sulphuryl chloride reacts with a solution of ethyl acetonedioxalate in dry ether, yielding *ethyl dichlorochelidonate*, $C_{11}H_{10}O_6Cl_2$, which crystallises from methyl alcohol in glistening prisms melting at 137—138°. A by-product is *ethyl chlorochelidonate*, $C_{11}H_{11}O_6Cl$, melting at 77°. The separation of the mono- and di-chloro-derivatives is difficult. Iodine reacts with an acetic acid or acetone solution of ethyl acetonedioxalate, yielding a product free from halogen. It decomposes above 250°, is soluble in alkalis, and its analytical data agree with the formula $C_{14}H_{12}O_{16}$.

J. J. S.

New Reactions of some Hydrols. Robert Fosse (*Bull. Soc. chim.*, 1906, [iii], 35, 1005—1017. Compare this vol., i, 691, 756).—Xanthydrol, $OH\cdot CH<\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}>O$, condenses with hydroxylamine, forming a *product*, $C_{13}H_{11}O_2N$, which crystallises in needles, and, on treatment with a solution of hydrogen chloride in alcohol, yields hydroxylamine hydrochloride and *xanthyl chloride*,



$CH\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}OCl$,

which is unstable and reacts with alcohol, yielding xanthen,

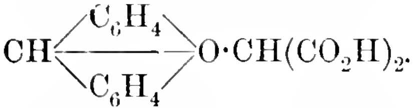
$$CH_2<\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}>O,$$

and acetaldehyde. The substance $C_{13}H_{11}O_2N$ begins to melt at 140° and at 150° is decomposed, yielding *dixanthyl*,

$$O<\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}>CH\cdot CH<\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}>O,$$

which crystallises in needles and melts at 204—205°. Xanthydrol also reacts with semicarbazide, yielding a *product*, $C_{14}H_{13}O_2N_3$, which melts and decomposes at 170—171° and reacts with hydrogen chloride in alcohol in much the same way as the oxime described above.

With malonic acid in acetic acid, xanthydrol condenses to form *xanthylmalonic acid*, which is provisionally represented by the formula



$CH\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}O\cdot CH(CO_2H)_2$. This crystallises in brilliant, silvery tablets, decomposes at 140°, forming a green liquid, is decomposed by hydrogen bromide in acetic acid, forming *xanthyl bromide* and malonic acid, and by hydrogen chloride in alcohol, yielding xanthen, acetaldehyde and malonic acid. When heated with pyridine, it furnishes xanthylacetic acid, $O<\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}>CH\cdot CH_2\cdot CO_2H$, which is not attacked by the halogen acids.

Dinaphthapyrylmalonic acid, $CH<\genfrac{}{}{0pt}{}{C_{10}H_6}{C_{10}H_6}>O\cdot CH(CO_2H)_2$, obtained by the action of malonic acid on dinaphthapyranol or dinaphthapyryl bromide, is decomposed by hydrogen chloride into malonic acid and dinaphthapyryl chloride, and by pyridine into dinaphthapyrylacetic acid and carbon dioxide.

Xanthylcyanoacetic acid, similarly obtained, decomposes at 164—166°. It is decomposed by hydrogen bromide in acetic acid, yielding xanthyl bromide and cyanoacetic acid, and with pyridine furnishes *xanthylacetonitrile* which melts at 140°.

p-*Methoxyphenyl-α-naphthyl-β-propionic acid*,

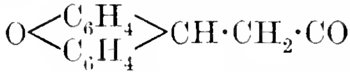
$$C_{10}H_7\cdot CH(C_6H_4\cdot OMe)\cdot CH_2\cdot CO_2H,$$

obtained by condensing malonic acid with *p*-methoxyphenyl-*α*-naphthylcarbinol, furnishes a p-*toluidide*, which melts at 176—177°. 3 : 4-*Methyl-*

enedioxyphenyl-α-naphthyl-β-propionic acid, prepared similarly, melts at 205°. p-*Dimethylaminophenyl-α-naphthyl-β-propionic acid* melts at 183°. pp-*Tetramethyldiaminodiphenyl-β-propionic acid*,

$$CH(C_6H_4\cdot NMe_2)_2\cdot CH_2\cdot CO_2H,$$

obtained from Michler's hydrol, melts at 222°. Triphenylcarbinol, when fused with malonic acid, yields triphenyl-β-propionic acid. Cyanoacetic acid condenses with *p*-methoxyphenyl-α-naphthylcarbinol to form an *acid*, $C_{21}H_{17}O_3$, and a similar *product* is obtained on condensation with Michler's hydrol. Triphenylcarbinol and cyanoacetic acid gives (1) a *product*, $C_{22}H_{17}O_2N$, which crystallises in colourless needles and melts and decomposes at 155°, and (2) a neutral, nitrogenous *substance* which melts at 114—115°. Benzhydrol reacts with cyanoacetic acid to form a nitrogenous *compound*, insoluble in acids, which melts at 144—155°.

[With N. Robyn.]—A large number of inorganic salts of the above acids have been prepared and analysed. The condensation products of these with β-ketonic esters (this vol., i, 756), when heated with acetic acid in a closed tube, yield ketones, thus ethyl xanthylacetoacetate furnishes *xanthylpropanone*,  $O<\substack{C_6H_4\\C_6H_4}>CH\cdot CH_2\cdot COMe$, which crystallises from light petroleum in slender needles and melts at 101—102°. *Xanthylacetophenone*, similarly obtained from ethyl xanthylbenzoylacetate, forms small, white crystals and melts at 83—84°.

[With M. Baillon.]—*Xanthylacetanilide* forms long, silky needles and melts at 213—214°. *Xanthylaceto*-o-*toluidide* crystallises in slender needles and melts at 215—216°; the *meta-isomeride* melts at 153—154°, and the *para*-compound at 204—205°. *Xanthylaceto-α-naphthalide* melts at 210—211°, and the *β-isomeride* at 225—216°.

T. A. H.

Alkaloids of Calumba Root. Johannes Gadamer (*Arch. Pharm.*, 1906, **244**, 255—256. Compare Abstr., 1903, i, 50).—An introduction to the following paper, and to one by K. Feist that will appear shortly.

C. F. B.

Alkaloids of Calumba Root. E. Günzel (*Arch. Pharm.*, 1906, **244**, 257—269. Compare Gadamer, Abstr., 1903, i, 50).—From an alcoholic extract of the root the alcohol was distilled; the residue was diluted with a little water and much alcohol; ether was added, producing a viscid precipitate; the solution was filtered and evaporated, and the residue dissolved in water and shaken with ether, which dissolved fatty substances and columbine. The aqueous liquid was freed from alcohol and ether by heating, clarified with kieselguhr, and precipitated with potassium iodide; from the precipitate the *iodide* melting at 210°, of an alkaloid "B" was extracted by boiling with alcohol, and columbamine iodide remained.

Columbamine iodide, probably, $C_{21}H_{22}O_5NI = C_{17}H_{10}ONI(OMe)_4$, is yellow and melts at 224°; the corresponding *chloride* crystallises with $2\frac{1}{2}H_2O$ in yellow needles melting at 194°, and with $4H_2O$ in brown prisms melting at 184°; the *hydrogen sulphate* melts at 220—222°; a crystalline aurichloride, platinichloride, and nitrate were prepared but not analysed; a greenish-black crystalline pentasulphide,

$$(C_{21}H_{22}O_5N)_2S_5,$$

melting at 139°, was obtained from the iodide by the action of yellow aqueous ammonium sulphide (compare Schreiber, *Arch. Pharm.*, 1890, **228**, 631; Abstr., 1890, 1012). The iodide is reduced in aqueous solution by zinc and sulphuric acid to the iodide of a base $C_{21}H_{25}O_5N = C_{17}H_{13}ON(OMe)_3$, *tetrahydrocolumbine*, which melts at 142° and is sensitive to light and air; the *platinichloride* of this mono-acid base melts at 228°; the chloride and aurichloride, the latter melting at 201°, were prepared but not analysed. C. F. B.

Quinine Formates. P. Guigues (*J. Pharm. Chim.*, 1906, [vi], **24**, 301—302. Compare Abstr., 1905, i, 811).—*Quinine formate*,

$$C_{20}H_{24}O_2N_2,2HCO_2H,$$

obtained by neutralising a solution of quinine or quinine sulphate in excess of dilute formic acid with ammonia solution, is very soluble in water, melts below 100°, and loses some formic acid.

A *basic quinine formate*, $C_{20}H_{24}O_2N_2,HCO_2H$, is obtained by dissolving quinine in the requisite quantity of formic acid and adding ammonium formate to the solution. This does not decompose when heated at 100° and dissolves in less than 20 parts of water. T. A. H.

New Salt of Quinine. Luigi Santi (*Chem. Centr.*, 1906, ii, 1205—1206; from *Boll. Chim. Farm.*, 1906, **45**, 557—560).—On mixing together ethereal solutions of pure quinine, $C_{20}H_{24}O_2N_2,3H_2O$, and of acetylsalicylic acid and leaving the mixture for twelve hours, a quantitative yield of a salt is obtained which has the composition $OAc\cdot C_6H_4\cdot CO_2H,C_{20}H_{24}O_2N_2$. This substance which is insoluble in ether but dissolves readily in alcohol or chloroform melts at 157°. P. H.

Thioquinine and Thiocinchonine. Ezio Comanducci and Luigi Pescitelli (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1906, [iii], **12**, 280—285).—*Thioquinine*, $(C_{20}H_{23}ON_2)_2S$, prepared by the action of phosphorus pentasulphide on quinine in chloroform solution, separates from alcohol as a yellow, micro-crystalline powder melting at 150—152° and is soluble in chloroform and sparingly so in ether. It has an odour resembling that of onions and it dissolves in nitric or sulphuric acid, giving a blue fluorescence. With chlorine or bromine water and ammonia it gives the thalleioquinine reaction, and with chlorine water, potassium ferrocyanide, and ammonia it yields a red coloration. When dissolved in dilute sulphuric acid and treated with acetic acid, alcohol, and tincture of iodine, it gives the herapathite reaction. In boiling chloroform solution, it has the normal molecular weight.

Thiocinchonine, $(C_{19}H_{21}N_2)_2S$, prepared by the action of phosphorus pentasulphide on cinchonine, is deposited from alcohol as an amorphous powder having an odour like that of garlic, and decomposes, without melting, at about 130°. It dissolves in chloroform, in which it exhibits normal ebullioscopic behaviour, and, to a slight extent, in ether.

T. H. P.

Extraction of Coca Leaves. ANNE W. K. DE JONG (*Rec. trav. chim.*, 1906, **25**, 311—329. Compare Abstr., 1905, ii, 778; this vol., ii, 315, 625).—In the industrial process for the extraction of the alkaloids from Peruvian coca leaves, the leaves in a fine state of division are treated with a mixture of dilute sodium carbonate solution and petroleum, the petroleum solution of the alkaloids is then neutralised with dilute hydrochloric acid, and the aqueous solution of the hydrochlorides of the alkaloids decomposed by sodium carbonate and the alkaloids extracted by petroleum. The author finds that the best results are obtained when ammonia is used instead of sodium carbonate, and ether instead of petroleum in the above method of extraction; from an exhaustive series of experiments (for details of which the original must be consulted) it is shown that the percentage of the total alkaloid extracted depends on: (1) the action of excess of sodium carbonate, ammonia, or hydrochloric acid on the alkaloids, (2) the solubility of the alkaloids in the petroleum, (3) the quantities of sodium carbonate and of water, (4) the quantity of petroleum and the duration of the extraction, (5) the state of division of the leaves, and (6) the quantities of hydrochloric acid and sodium carbonate or ammonia employed in the last stage of the process. Comparative experiments conducted on fresh leaves and dried leaves showed that whilst 3 kilos. of the fresh leaves yielded 6·65 grams of alkaloids, the same weight of leaves after drying yielded 10·65 grams. M. A. W.

Ephedrine and ψ-Ephedrine. ERNST SCHMIDT and HERMANN EMDE (*Arch. Pharm.*, 1906, **244**, 241—255).—ψ-Ephedrine, obtained from ephedrine (E. Schmidt, this vol., i, 602), was found to be identical with the natural base in rotation ($[\alpha]_D$ 51·2° at 20°, in 0·5 per cent. alcoholic solution) and crystalline form (rhombic system; $a:b:c = 0·843:1:1·858$). Ephedrine undergoes a partial transformation when it is heated by itself at 100°, or with aqueous sodium carbonate.

When ψ-ephedrine is heated with methyl-alcoholic methyl iodide it is converted partially into oily *methyl-ψ-ephedrine*, the *aurichloride* of which, $C_{11}H_{17}ON,HAuCl_4$, melts at 119—123°. When excess of methyl iodide is used, the quaternary *methiodide*, $C_{12}H_{20}ONI$, melting at 205°, is obtained in addition; the corresponding quaternary *aurichloride* and *platinichloride* melt at 194—195° and 204—205° respectively. These salts differ distinctly, although often only slightly, from the corresponding salts derived from ephedrine; and the quaternary iodide crystallises in the rhombic system ($a:b:c = 0·642:1:1·209$) whilst the quaternary iodide from ephedrine is rhombic with sphenoidal hemihedry ($a:b:c = 0·979:1:0·761$); again, ψ-ephedrine hydriodide, melting at 172°, is rhombic and holohedral ($a:b:c = 0·603:1:1·372$), whilst ephedrine hydriodide, melting at 155—156°, although rhombic, is hemihedral (0·737 : 1 : 0·286).

Methyl-ψ-ephedrine methyl hydroxide, when subjected to prolonged distillation with water, decomposes into trimethylamine and an unsaturated *substance*, $C_9H_{10}O$, which boils at 197—199°. A similar result is obtained with methylephedrine methyl hydroxide, except that the unsaturated substance boils at 212—216°, and possibly is identical with α-phenylallyl alcohol, $CH_2{:}CH{\cdot}CHPh{\cdot}OH$.

A formula suggested as possible for ephedrine is

$$NHMe{\cdot}CHMe{\cdot}CHPh{\cdot}OH.$$

C. F. B.

Ergot. Friedrich Krafft (*Arch. Pharm.*, 1906, **244**, 336—359).—The following substances were isolated: A phytosterol: ergosterol (Tanret). Two alkaloids: ergotinine (Tanret; Keller's "cornutine" and Jakobi's "secaline"); and *hydroergotinine*, which is isomorphous and more soluble. A crystalline δ-lactonic acid, *secalonic acid*, $C_{14}H_{14}O_6$, which is yellow and melts at 244°; and the corresponding *hydroxy*-acid, and another *acid* formed by loss of carbon dioxide, both of which are yellow and amorphous. *Aminosecalesulphonic acid* (Kobert's "ergotic acid"), $NH_2{\cdot}C_{15}H_{27}O_{15}{\cdot}SO_3H$. Betaine, choline and mannitol.

The alkaloids are poisons, causing convulsions and gangrene, but they do not cause the specific action of the drug on the uterus.

C. F. B.

Ergotinine. Charles Tanret (*J. Pharm. Chim.*, 1906, [vi], **24**, 397—403).—Since ergotinine combines with phenol, the use of the latter as a solvent for cryoscopic determinations of the molecular weight of ergotinine is not permissible (see Barger and Carr, *Pharm. J.*, 1906, [iv], **23**, 257). From the analysis of its salts, the formula $C_{35}H_{40}O_5N_5$ is deduced. The use of the name ergotoxine, applied by Barger and Carr (*loc. cit.*) to amorphous ergotinine, is objected to. E. F. A.

Hordenine. Otto Gaebel (*Arch. Pharm.*, 1906, **244**, 435—441. Compare Léger, this vol., i, 204, 761).—Hordenine, $C_{10}H_{15}ON$, is oxidised completely by permanganate. If it is methylated by shaking a solution of it in aqueous potassium hydroxide with dimethyl sulphate, and the resulting alkaline solution oxidised with potassium permanganate on the water-bath, anisic acid is obtained. When the methiodide is treated with silver hydroxide, and the quaternary ammonium hydroxide which results is submitted to dry-distillation, trimethylamine is among the products. The formula,

$$OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_2\ [OH : CH_2 = 1 : 4],$$

is the only one which expresses these reactions of hordenine satisfactorily. C. F. B.

Alkaloids of Tobacco. Amé Pictet (*Arch. Pharm.*, 1906, **244**, 375—389).—A complete account of researches already published (Abstr., 1895, i, 627; 1898, i, 50, 688; 1899, i, 164; 1900, i, 685; 1901, i, 339; 1904, i, 86, 520, 771; 1905, i, 545, 543).

The subjects dealt with are:—Constitution of nicotine; synthesis of nicotine; nicoteine; nicotimine; nicotelline; pyrrolidine. C. F. B.

Opium Alkaloids and the Constitution of Berberine and Morphine. Franz Faltis (*Chem. Centr.*, 1906, ii, 1011—1012; from *Pharm. Post*, **39**, 497—499).—The author discusses the common origin of the alkaloids papaverine, narcotine, berberine, corydaline, morphine, codeine, thebaine, protopine, glaucine, and chelidonine, and arrives at conclusions different from those of Perkin, Pschorr, and Freund as to the formulæ of berberine and morphine. P. H.

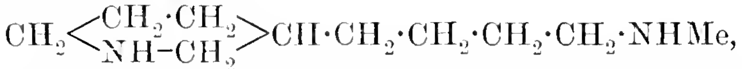
Reduction of Metanicotine with Sodium and Absolute Alcohol. II. EMIL MAAS and ADOLF HILDEBRANDT (*Ber.*, 1906, **39**, 3697—3702. Compare Abstr., 1905, i, 543).—The product, obtained by reducing metanicotine by means of sodium and absolute alcohol, is not uniform, but a mixture of hexahydrometanicotine and octahydrometanicotine, which may be separated by fractional distillation in a current of steam.

Hexahydrometanicotine,

$$CH_2<\begin{matrix}CH_2\cdot CH_2\\ NH-CH_2\end{matrix}>CH\cdot CH{:}CH\cdot CH_2\cdot CH_2\cdot NHMe,$$

is an oil which boils at 248—250°, has the sp. gr. 0·9578 at 20°/4°, and is volatile with steam. It is optically inactive. The *platinichloride*, $C_{10}H_{20}N_2,H_2PtCl_6$, melts and decomposes at 225°.

Octahydrometanicotine,



$$CH_2<\begin{matrix}CH_2\cdot CH_2\\ NH-CH_2\end{matrix}>CH\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot NHMe,$$

is an oil which boils at 258·5—260°; it is also volatile with steam. It has the sp. gr. 0·9173° at 20°/4°, and is optically inactive. Its *hydrochloride*, $C_{10}H_{22}N_2,2HCl$, separates from water in glistening, colourless needles and melts at 202°; the *platinichloride*,

$C_{10}H_{22}N_2,H_2PtCl_6$,

melts and decomposes at 202·5°; the *aurichloride*, $C_{10}H_{22}N_2,2HAuCl_4$, melts at 142°. A. McK.

Solanine Extracted from Solanum sodomœum. GIUSEPPE ODDO and AMEDEO COLOMBANO (*Atti R. Accad. Lincei*, 1906, [v], **15**, ii, 312—319. Compare this vol., i, 527).—The melting point of solanine varies considerably with the size of the flame by which it is heated, so that it cannot be used as a criterion of purity.

The authors have effected greater purification of solanine by crystallising it several times from 80 per cent. alcohol, then dissolving it in very dilute sulphuric acid, filtering, precipitating by means of alcohol sodium hydroxide and washing with water until all the alkali is removed. After repetition of this process and further crystallisation from alcohol, the solanine obtained gives, on analysis and molecular weight determination in acetic acid, numbers agreeing well with the formula $C_{27}H_{47}O_9N,\frac{1}{2}H_2O$. T. H. P.

Amino-derivatives of Tetraphenylethylene. Quinonoid Compounds. X. RICHARD WILLSTÄTTER and MAX GOLDMANN (*Ber.*, 1906, **39**, 3765—3776).—s-4 : 4′-*Tetramethyldiaminotetraphenylethylene*,

$NMe_2\cdot C_6H_4\cdot CPh{:}CPh\cdot C_6H_4\cdot NMe_2$,

prepared by reduction of *p*-dimethylaminobenzophenone with tin and hydrochloric acid in alcoholic solution, crystallises on addition of ether or light petroleum to its solution in benzene or chloroform in long, glistening, lemon-yellow needles, melts at 224—225°, decomposes above 300°, and gives a deep-red coloration with ferric chloride in acid solutions. The *hydrochloride* and *sulphate* form colourless needles, the dark reddish-brown *mercurichloride* and *platinichloride* are insoluble.

When reduced by means of zinc dust in glacial acetic acid solution, *p*-dimethylaminobenzophenone yields s-4 : 4′-*tetramethyldiaminotetraphenylethyleneglycol*, $NMe_2\cdot C_6H_4\cdot CPh(OH)\cdot CPh(OH)\cdot C_6H_4\cdot NMe_2$, which crystallises in slender spears, melts and decomposes at 186—187°, becomes yellow on exposure to light, and dissolves in concentrated hydrochloric acid, forming a colourless solution which becomes red slowly at the ordinary temperature or more quickly when heated. When reduced with zinc dust and glacial acetic acid, the pinacone yields tetramethyldiaminotetraphenylethylene and a *substance*, which is obtained also by the action of concentrated sulphuric acid on the pinacone, crystallises in colourless, rhombic and octagonal leaflets, melts at 255—256°, has feeble basic properties, and does not give a coloration with ferric chloride in acid solutions.

When boiled with absolute alcohol, the pinacone yields a *pinacoline*, $C_{30}H_{30}ON_2$, which crystallises in rhombic plates, melts at about 214—217°, and forms a *hydrochloride* crystallising in long, silky, hexagonal leaflets.

p-*Dimethylaminobenzylhydrol ethyl ether*, $NMe_2{\cdot}C_6H_4{\cdot}CHPh{\cdot}OEt$, prepared by the action of alcohol on the benzhydrol in presence of an acid, crystallises in colourless needles, melts at 37—37·5°, boils at 206—208° under 14 mm. pressure, has a slight odour of benzaldehyde, and gives with hot concentrated hydrochloric acid an intense yellow, with concentrated sulphuric acid an intense red, coloration.

4-*Dimethylaminobenzophenone*-3 *sulphonic acid*,

$$COPh{\cdot}C_6H_3(NMe_2){\cdot}SO_3H,H_2O,$$

formed by the action of fuming sulphuric acid on the ketone at 130°, separates in large, clear, triclinic crystals [$a:b:c = 1{\cdot}1310:1:2{\cdot}8296$; $\alpha = 89°1{\cdot}5'$, $\beta = 83°40'$, $\gamma = 77°31'$], loses H_2O over sulphuric acid, melts and decomposes at 296—298°, forms yellow solutions, has a strong acid reaction, reduces hot ammoniacal silver solution, and decolorises potassium permanganate in alkaline or acid solution. The *barium*, *calcium*, and *silver* salts are described. The *oxime*, $C_{15}H_{16}O_4N_2S$, crystallises in glistening, white needles, effloresces on exposure to air, and melts and decomposes at 296—298°. When reduced with tin and concentrated hydrochloric acid, the sulphonic acid yields s-4 : 4′-*tetramethyldiaminotetraphenylethylene*-3 : 3′-*disulphonic acid*,

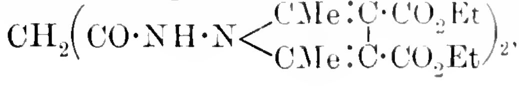
$$SO_3H{\cdot}C_6H_3(NMe_2){\cdot}CPh{:}CPh{\cdot}C_6H_3(NMe_2){\cdot}SO_3H,$$

which is purified by recrystallisation of its *calcium* salt. The acid crystallises in two modifications: in colourless, rhombic plates or leaflets containing $2H_2O$ on slow cooling of the aqueous solution; and in long, white needles on rapid separation from the solution. The latter form effloresces on exposure to air. With acid or neutral oxidising agents the disulphonic acid gives an intense blood-red coloration which is destroyed by reducing agents or alkali hydroxides. The *salts* are yellow.

Reduction of Michler's ketone with tin and concentrated hydrochloric acid leads to the formation of octamethyltetra-aminotetraphenylethylene (Gattermann, Abstr., 1896, i, 172). G. Y.

Condensation Products of the Dihydrazides of Dibasic Acids.

CARL BÜLOW and R. WEIDLICH (*Ber.*, 1906, 39, 3372—3377).—*Ethyl malonyl-bis*-[1-*amino*-2 : 5-*dimethylpyrrole*-3 : 4-*dicarboxylate*],



$CH_2\left(CO{\cdot}NH{\cdot}N{<}\begin{matrix}CMe{:}C{\cdot}CO_2Et\\ \vert\\ CMe{:}C{\cdot}CO_2Et\end{matrix}\right)_2$, prepared by the interaction of malonyldihydrazide and ethyl diacetylsuccinate in glacial acetic acid solution, crystallises in bundles of needles melting at 122°. *Malonyldiacetyldihydrazide*, $C_7H_{12}O_1N_4$, is a white powder melting at 228°.

Diacetophenonemalonyldihydrazone,

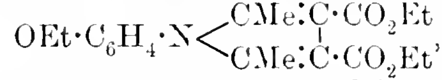
$$CPhMe:N\cdot NH\cdot CO\cdot CH_2\cdot CO\cdot NH\cdot N:CPhMe,$$

prepared from malonyldihydrazide and acetophenone, melts at 221°; *methyl malonyldihydrazide* melts at 179°, and condenses with ethyl diacetylsuccinate to form *ethyl methylmalonyl-bis-*[1*-amino-*2 : 5*-dimethylpyrrole-*3 : 4*-dicarboxylate*] melting at 139—140°. *Dibenzaldehyde methylmalonyldihydrazone* melts at 249°, *methyl malonyldiacetyldihydrazide* at 225°. Succinyldihydrazide melts at 166° (compare Curtius, Abstr., 1895, i, 263), the *diacetyl* derivative at 233°. *Ethyl succinyl-bis-*[1*-amino-*2 : 5*-dimethylpyrrole-*3 : 4*-dicarboxylate*] melts at 173°.

E. F. A.

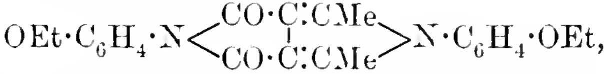
Action of Ethyl Acetylsuccinate and Diacetylsuccinate on Phenetidine. Luciano Rossi (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1906, [iii], **12**, 299—308).—When phenetidine reacts with ethyl acetylsuccinate or diacetylsuccinate, the ketonic group of the latter enters into reaction more readily than the carboxyl group, a fact which indicates that these compounds have the enolic structure.

The interaction of ethyl diacetylsuccinate (1 mol.) and phenetidine (1 mol.) yields: (1) *ethyl* 1-p*-ethoxyphenyl-*2 : 5*-dimethylpyrrole-*3 : 4*-dicarboxylate*,



$$OEt\cdot C_6H_4\cdot N<\begin{matrix}CMe:C\cdot CO_2Et\\ |\\ CMe:C\cdot CO_2Et\end{matrix},$$

which crystallises from alcohol in microscopic, yellow prisms and from acetic acid or benzene in stellar aggregates of needles melting at 155—156°; it has a neutral reaction, dissolves in ether, acetone, or ethyl acetate, gives the pyrrole reaction, and, when dissolved in alcohol, yields an intense blue coloration with ferric chloride; (2) the p*-ethoxyanil*,



$$OEt\cdot C_6H_4\cdot N<\begin{matrix}CO\cdot C:CMe\\ |\\ CO\cdot C:CMe\end{matrix}>N\cdot C_6H_4\cdot OEt,$$

of the foregoing acid; this crystallises from alcohol in tufts of minute, faintly yellow needles melting at 272°, and dissolves sparingly in ether, acetone, benzene, acetic acid, or ethyl acetate; it is a neutral substance and gives the pyrrole reaction, but yields no coloration with ferric chloride.

The interaction of 1 mol. of ethyl diacetylsuccinate and 2 mols. of phenetidine yields: (1) the compound melting at 272° (*vide supra*) (2) *Ethyl ββεε-tetra-*p*-phenetidinohexane-γδ-dicarboxylate*,

$$C_2H_2(CO_2Et)_2[CMe(NH\cdot C_6H_4\cdot OEt)_2]_2,$$

which separates from alcohol as a yellow, microcrystalline powder melting at 159—160°, dissolves sparingly in ether, acetone, benzene, ethyl acetate, or acetic acid, and has a neutral reaction.

The action of 1 mol. of ethyl diacetylsuccinate on 4 or 6 mols. of phenetidine yields: (1) the compound melting at 159—160° (*vide supra*); (2) *ββεε-tetra-*p*-phenetidinohexane-γδ-dicarboxyphenetidide*,

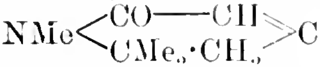
$$C_2H_2(CO\cdot NH\cdot C_6H_4\cdot OEt)_2[CMe(NH\cdot C_6H_4\cdot OEt)_2]_2,$$

which crystallises from alcohol in white needles melting at 230°, dissolves moderately readily in acetone and sparingly in ether, benzene, ethyl acetate, or acetic acid, and has a neutral reaction.

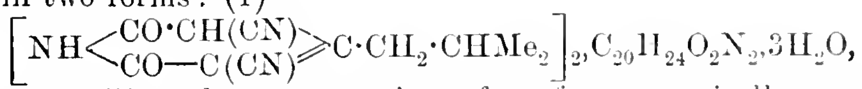
The action of ethyl acetylsuccinate on phenetidine yields: (1) *ethyl γγ-di-p-phenetidinobutane-αβ-dicarboxylate*,

$$\mathrm{CO_2Et{\cdot}CH_2{\cdot}CH(CO_2Et){\cdot}CMe(NH{\cdot}C_6H_4{\cdot}OEt)_2},$$

which separates from alcohol in white crystals melting at 114—115°, dissolves in benzene, acetone, or acetic acid, has a neutral reaction, and in cold alcoholic solution gives a green coloration with ferric chloride; (2) *γγ-Diphenetidinobutane-αβ-dicarboxyphenetidide*, $\mathrm{OEt{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}CH(CO{\cdot}NH{\cdot}C_6H_4{\cdot}OEt){\cdot}CMe(NH{\cdot}C_6H_4{\cdot}OEt)_2}$, which separates from alcohol in white crystals melting at 230—232°, dissolves sparingly in benzene, acetic acid, or ethyl acetate, and has a neutral reaction. T. H. P.

New Acid of the Tetrahydropyridine Series (2-Oxy-1 : 6 : 6-trimethyl-Δ^3-tetrahydropyridine-4-carboxylic Acid). GALEAZZO PICCININI (*Atti R. Accad. Sci. Torino*, 1906, **41**, 1019—1043).—*2-Oxy-1 : 6 : 6-trimethyl-Δ^3-tetrahydropyridine-4-carboxylic acid*,  $\mathrm{NMe}{<}\begin{matrix}\mathrm{CO{-\!-\!-}CH}\\ \mathrm{CMe_2{\cdot}CH_2}\end{matrix}{>}\mathrm{C{\cdot}CO_2H}$, prepared by the action of permanganate on 3-cyano-1 : 4 : 6 : 6-tetramethylpyridone in neutral solution, crystallises from water in colourless or pale rose-coloured, striated prisms melting at 174—174·5° (corr.), has the normal molecular weight in boiling acetone, and dissolves readily in alcohol, benzene, ethyl acetate, acetic acid, or chloroform, and sparingly in ether. It behaves as a monobasic acid towards alkali hydroxides or carbonates, and, when heated at 290—300°, it evolves methane. It dissolves unchanged in concentrated hydrochloric, sulphuric, or nitric acid, and in aqueous solution it hydrolyses sucrose. It gives with even very dilute ferric chloride solutions an intense blood-red coloration; with dilute ferrous sulphate solution an intense blood-red coloration. The *sodium* ($+\mathrm{H_2O}$) and *barium* salts of the acid were analysed. The 3 : 5-*dibromo*-derivative, $\mathrm{C_9H_{11}O_3NBr_2}$, separates from benzene in colourless, prismatic crystals melting at 137—139°, dissolves slightly in water and gives no red coloration with ferric chloride. The isomeric 5 : 5-*dibromo*-derivative crystallises from benzene with $\frac{1}{2}\mathrm{C_6H_6}$ in hard, heavy prisms, which effloresce in the air and melt at 201—202°, and its aqueous solution gives a blood-red coloration with ferric chloride; it dissolves readily in alcohol, ether, chloroform, or benzene, and sparingly in carbon disulphide or water, and on heating at its melting point or on boiling with water it loses all its bromine, in the latter case as hydrogen bromide. When heated with potassium hydroxide at 300—320° under a pressure of 40 mm., the acid decomposes, yielding methylamine, oxalic acid, a neutral substance, a syrupy nitrogenous acid, and acrylic acid (?). T. H. P.

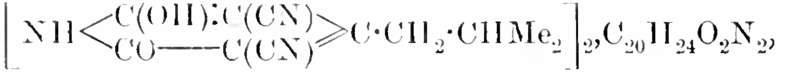
Transformations of the Quinine Salt of *iso*Butyldicyanoglutaconimide. SILVIO ZUBLENA (*Atti R. Accad. Sci. Torino*, 1906, **41**, 1044—1053).—The quinine salt of *iso*butyldicyanoglutaconimide exists in two forms: (1)



$$\left[\mathrm{NH}{<}\begin{matrix}\mathrm{CO{\cdot}CH(CN)}\\ \mathrm{CO{-}C(CN)}\end{matrix}{\gtrless}\mathrm{C{\cdot}CH_2{\cdot}CHMe_2}\right]_2,\mathrm{C_{20}H_{24}O_2N_2,3H_2O},$$

which crystallises from water in tufts of concentrically-arranged, intensely yellow, slender prisms, and melts and decomposes at about

282°. If this salt, in either the hydrated or the dehydrated form, is suspended in water, it gradually changes into (2) a more stable and less soluble anhydrous modification,



$$\left[\mathrm{NH}{<}\begin{matrix}\mathrm{C(OH){:}C(CN)}\\ \mathrm{CO{-\!-\!-}C(CN)}\end{matrix}{>}\mathrm{C{\cdot}CH_2{\cdot}CHMe_2}\right]_2,C_{20}H_{24}O_2N_2,$$

which separates in colourless, probably triclinic, microscopic prisms. This change is accelerated by the action of light. The colourless modification begins to turn yellow at 200°, and, like the yellow form, melts and decomposes at about 282°. A solution of the colourless salt in 60 or 95 per cent. alcohol deposits the yellow modification.

T. H. P.

Dioximes and similar Compounds. LEO TSCHUGAEFF (*Ber.*, 1906, **39**, 3382—3389; *J. Russ. Phys. Chem. Soc.*, 1906, **38**, i, 7—9. Compare Abstr., 1905, i, 743).—The behaviour of different metallic solutions towards the stereoisomeric oximes derived from 2-benzoylpyridine and the oxime of 4-benzoylpyridine (Tschitschibabin, Abstr., 1902, i, 175) has been investigated. The only oxime which give colorations or precipitates is the 2-benzoylpyridineoxime melting at 150—152°, and hence the *syn*-configuration, $\begin{matrix}\mathrm{C_5NH_5{\cdot}C{\cdot}Ph,}\\ \mathrm{HO{\cdot}\ddot{N}}\end{matrix}$ is assigned to it.

The *palladium* compound, $C_{24}H_{18}O_2N_4Pd$, obtained by the action of palladium ammonium chloride on an alcoholic solution of the oxime, crystallises in canary-yellow needles, sparingly soluble in alcohol or ether. It may be recrystallised from chloroform, and is not decomposed by dilute alkalis or weak acids. The *platinum* derivative,

$$C_{24}H_{18}O_2N_4Pt,$$

prepared by the action of platinum pyridine chloride on the oxime, forms dark yellow crystals.

Thiele's nitrosoguanidine, represented by the tautomeric formula $NH{:}C(NH_2)N{:}N{\cdot}OH$, also yields metallic derivatives. Structural formulæ for the metallic compounds are given.

J. J. S.

Quinoline Derivatives. II. Nitration of Quinoline and its Mononitro-derivatives. ADOLF KAUFMANN and HERMAN DECKER (*Ber.*, 1906, **39**, 3648—3651. Compare Claus and Kramer, Abstr., 1885, 908; Claus and Hartmann, Abstr., 1896, i, 391; Claus and Schnell, *ibid.*, 319).—6-Nitroquinoline may be further nitrated when heated with the theoretical amount of potassium nitrate and concentrated sulphuric acid at 130—140° for ten hours. The product is a mixture of 5 : 8-dinitroquinoline and an isomeric compound melting at 185°. The latter dissolves readily in most organic solvents and in dilute sodium hydroxide solution; it does not react with methyl iodide and is readily sublimed.

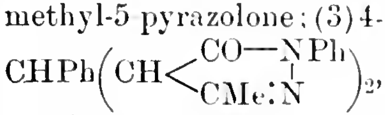
7-Nitroquinoline is readily nitrated when heated with fuming nitric and concentrated sulphuric acid, the chief product being a new dinitroquinoline melting at 225°. It sublimes readily and dissolves in sodium hydroxide to a characteristic yellow solution. A second product is a dinitro-compound melting at 175°, probably identical with 5 : 7-dinitroquinoline.

8-Nitroquinoline when boiled for twenty hours with a mixture of

nitric and sulphuric acid, yields 6 : 8-dinitroquinoline, identical with the product obtained from 2 : 4-dinitroaniline (La Coste, Abstr., 1882, 979).
J. J. S.

Diphenylhydrazones of a Series of Aldehydes. A. D. MAURENBRECHER (*Ber.*, 1906, **39**, 3583—3587. Compare Clowes and Tollens, Abstr., 1900, ii, 56).—The *diphenylhydrazones* of the following aldehydes are described; the formulæ and crystalline forms are those of the hydrazones; the temperatures are melting points. Formaldehyde, $C_{13}H_{12}N_2$, white plates, 34·5—35°; propaldehyde, $C_{15}H_{16}N_2$, long, white needles, 20—21°; butaldehyde, $C_{16}H_{18}N_2$, oil; *iso*butaldehyde, white plates, 30—30·5°; *iso*valeraldehyde, $C_{17}H_{20}N_2$, white plates or prisms, 36—36·5°; *o*-tolualdehyde, $C_{20}H_{18}N_2$, white needles, 103—104°; *m*-tolualdehyde, light yellow plates, 74—75°; *p*-tolualdehyde, white needles, 83—84°; cinnamaldehyde, $C_{21}H_{18}N_2$, yellow needles, 135—136°; cuminaldehyde, $C_{22}H_{22}N_2$, yellow needles, 78·5—79·5°; *o*-hydroxybenzaldehyde, $C_{19}H_{16}ON_2$, colourless needles, 138·5°; *m*-hydroxybenzaldehyde, yellow needles, 118—119°; vanillin, $C_{20}H_{18}O_2N_2$, violet leaflets, 130—131°; piperonal, $C_{20}H_{16}O_2N_2$, white plates, 134—135°.
G. Y.

Spontaneous Oxidation in presence of Benzaldehyde. MARIO BETTI (*Gazzetta*, 1906, **36**, ii, 427—433).—When dissolved in alcoholic ammonia in presence of a few drops of benzaldehyde or hydrogen peroxide or sodium peroxide, 1-phenyl-3-methyl-5-pyrazolone undergoes oxidation, yielding: (1) rubazonic acid; (2) 1-phenyl-4-benzylidene-3-methyl-5 pyrazolone; (3) 4-*benzylidene-bis*-1-*phenyl*-3-*methyl*-5-*pyrazolone*,



$$\mathrm{CHPh}\left(\mathrm{CH}<\begin{matrix}\mathrm{CO—NPh}\\ \mathrm{CMe{:}N}\end{matrix}\right)_2$$

which separates in shining, white crystals melting at 167°; the formation of this compound, together with benzaldehyde, from 1-phenyl-4-benzylidene-3-methyl-5 pyrazolone (2 mols.) and water is a reversible reaction. Whether the function of the benzaldehyde in the above reaction is merely to form hydrogen peroxide or some other peroxide or whether it takes part in a cycle of changes, at the end of which it is regenerated, is yet undecided.

On mixing alcoholic solutions of hydrobenzamide and 1-phenyl-3-methyl-5-pyrazolone, an *additive* compound,

$$\begin{matrix}\mathrm{NPh{\cdot}CO}\\ \mathrm{N{=}CMe}\end{matrix}>\mathrm{CH{\cdot}CHPh{\cdot}NH{\cdot}CHPh{\cdot}N{:}CHPh}\ (?),$$

is formed in shining, white prisms which turn yellow at 110° and melt and decompose at 125—126°. This compound may also be used in place of benzaldehyde for the oxidation of 1-phenyl-3-methyl-5 pyrazolone.
T. H. P.

New Additive Compounds of 1-Phenyl 2 : 3 dimethylpyrazolone (Antipyrine). FELICE GARELLI and G. A. BARBIERI (*Gazzetta*, 1906, **36**, ii, 168—172).—Contrary to Schuyten's statement (Abstr., 1898, i, 92, 452), an aqueous solution of the additive compound of antipyrine with zinc chloride gives a precipitate of zinc sulphide with ammonium sulphide. Solutions of the compounds formed by antipyrine with mercuric chloride, bromide, and cyanide give the same reactions as solutions of the mercuric haloid salts themselves. With ferric chloride, solutions of all the additive compounds of antipyrine yield the deep red coloration given by solutions of pure antipyrine.

Cryoscopic measurements of various additive compounds of antipyrine in water lead to the following values for the molecular weights, the true values of which are given in brackets: Antipyrine-mercuric cyanide, $Hg(CN)_2,C_{11}H_{12}ON_2$, 210—222 (440); antipyrine-quinol, $C_6H_4(OH)_2,2C_{11}H_{12}ON_2$, 151—171 (487); antipyrine-resorcinol,

$$C_6H_4(OH)_2,C_{11}H_{12}ON_2,$$

140—151 (298); antipyrine-chloral, $CCl_3{\cdot}CH(OH)_2,C_{11}H_{12}ON_2$, 178—183 (352). In aqueous solution, therefore, these compounds are completely resolved into their components.

The author is of opinion that the structural formulæ attributed to the double compounds formed by antipyrine have no greater value than the constitutional formulæ proposed for the natural silicates.

T. H. P.

Pyrimidines. XVIII. 5-Ethylcytosine. TREAT B. JOHNSON and GEORGE A. MENGE (*J. Biol. Chem.*, 1906, 2, 105—115. Compare Abstr., 1903, i, 526; this vol., i, 704).—*Ethyl sodioformylbutyrate*, $ONa{\cdot}CH{:}CEt{\cdot}CO_2Et$, is obtained by the condensation of ethyl formate and ethyl butyrate in the presence of sodium ethoxide. It reacts with ψ-ethylthiocarbamide, yielding 6-*oxy-2-ethylthiol-5-ethylpyrimidine*,

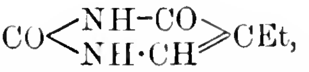
$$SEt{\cdot}C{<}\begin{matrix}NH{\cdot}CO\\N{-}CH\end{matrix}{>}CEt,$$

which crystallises from dilute alcohol in well-developed prisms melting at 119—120°. It dissolves readily in alcohol or benzene, but only sparingly in ether. An intermediate product in its formation is *βψ-ethylthiocarbamido-α-ethylacrylic acid*,

$$NH_2{\cdot}C(SEt){:}N{\cdot}CH{:}CEt{\cdot}CO_2H,$$

which crystallises in plates melting at 148—149°; at this temperature carbon dioxide is evolved and the pyrimidine derivative formed.

6-*Chloro-2-ethylthiol-5-ethylpyrimidine*, $C_8H_{11}N_2ClS$, boils at 160—163° under 24 mm. pressure and is readily converted into the corresponding oxy-derivative. 6-*Amino-2-ethylthiol-5-ethylpyrimidine*, $C_8H_{13}N_3S$, obtained by the action of alcoholic ammonia on the chloro-derivative at 130—140°, crystallises from a mixture of benzene and light petroleum in prisms melting at 74—76°.

2 : 6-*Dioxy-5-ethylpyrimidine* (*5-ethyluracil*),  $CO{<}\begin{matrix}NH{-}CO\\NH{\cdot}CH\end{matrix}{>}CEt$, is obtained by boiling the oxyethylthiol ethyl derivative with hydrobromic acid; it crystallises in microscopic prisms melting and decomposing at about 300°. One gram dissolves in 625 of water at 25°. 5-*Ethylcytosine hydrobromide*, $C_6H_9ON_3,HBr$, obtained by boiling the amino-ethylthiolethyl derivative with hydrobromic acid, crystallises in large prisms and melts and decomposes at 284—286°. 5-*Ethylcytosine*,

$$CO{<}\begin{matrix}N{:}C(NH_2)\\NH{-}CH\end{matrix}{>}CEt,$$

crystallises in slender, anhydrous prisms, melts and decomposes at 282—283° and dissolves in about 75 parts of water at 25°. It yields precipitates with mercuric chloride, phosphotungstic acid and potassium bismuthoiodide. The *platinichloride*, $(C_6H_9ON_3)_2,H_2PtCl_6,2H_2O$, dissolves readily in hot water, the *hydrochloride*, $C_6H_9ON_3,HCl$, crystallises in flat prisms and melts at 238—240°. The *nitrate* decomposes at 170—172°, and the *picrate* at 277—278°. Mixtures of basic hydrobromides have been obtained.

2 : 6-Dichloropyrimidine (Gabriel, Abstr., 1905, i, 182) may be obtained by heating 2-thiouracil (Wheeler and Bristol, *ibid.*, i, 483) with phosphorus pentachloride. J. J. S.

Preparation of 2-Arylimino-5 : 5-dialkylbarbituric Acids

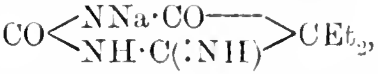
FARBWERKE VORM. MEISTER, LUCIUS, and BRÜNING (D.R.-P. 172979).—It has been found that the esters of the dialkylmalonic acids will condense with arylguanidines under the influence of alkali alkyloxides in methyl-alcoholic solution, but not in ethyl alcohol.

2-*Phenylimino*-5 : 5-*diethylbarbituric acid*, produced by condensing phenylguanidine nitrate and ethyl diethylmalonate with sodium methoxide in methyl-alcoholic solution, crystallises from acetic acid and melts at 249°.

2-*Phenylimino*-5 : 5-*dimethylbarbituric acid*, prepared in a similar way from methyl dimethylmalonate, crystallises from alcohol in well-defined needles and melts at 249—250°. 2-p-*Tolylimino*-5 : 5-*diethylbarbituric acid* crystallises in needles and melts at 239—240°. 2-o-*Tolylimino*-5 : 5-*diethylbarbituric acid* and 2-p-*chlorophenylimino*-5 : 5-*diethylbarbituric acid* melt at 230° and 276—277° respectively. These arylimino-derivatives, when hydrolysed with dilute acids, furnish the aromatic amine and the dialkylbarbituric acid. G. T. M.

Preparation of Imino-5 : 5-dialkylbarbituric Acids.

EMANUEL MERCK (D.R.-P. 172980. Compare Abstr., 1905, i, 179).—The iminodialkylbarbituric acids have already been obtained by condensing carbamide with the esters of cyanodialkylacetic acid in the presence of metallic alkyloxides. It is now found that the acyl derivatives of carbamide may be employed in this condensation, the condensing agent being sodium alkyloxide, sodamide, or even metallic sodium.

The *sodium* derivative,  $CO<\begin{matrix}NNa\cdot CO\text{——}\\ NH\cdot C(:NH)\end{matrix}>CEt_2$, of 4-imino-2 : 6-dioxy-5 : 5-diethylpyrimidine is obtained by condensing acetylcarbamide with ethyl cyanodiethylacetate in boiling alcoholic sodium ethoxide; the free pyrimidine is set free by acids. This condensation may also be effected by adding the cyanodialkylacetate to an intimate mixture of acetylcarbamide and sodamide suspended in xylene; the reagents are cooled at first, but finally heated at 120°. After removing the xylene, the product, on treatment with water, yields the sodium derivative of the iminodioxydialkylpyrimidine. G. T. M.

Preparation of 5 : 5-Dialkylbarbituric Acids.

FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 173241).—The 4-imino-6-oxy-2-thio-5 : 5-dialkylpyrimidines, when treated with an oxidising agent, lose their imino-group and sulphur atom, which are replaced by oxygen, so that a 5 : 5-dialkylbarbituric acid is produced. It is now shown that this substitution may be effected simply by boiling the thio-compound with an acid ; the change occurs in two stages, the imino-group being first removed, and then by further action the sulphur is eliminated. Fuming hydrochloric 40 per cent. sulphuric or 70 per cent. acetic acid may be used for this purpose, and in this way 4-imino-6-oxy-2-thio-5 : 5-dimethylpyrimidine and its diethyl- and dipropyl-homologues may be transformed into dimethyl-, diethyl-, and dipropyl-barbituric acids respectively. G. T. M.

Quinazolines. XVI. Synthesis of 6-Nitro-4-keto-2-methyldihydroquinazolines from 5-Nitroacetylanthranil and Primary Amines.

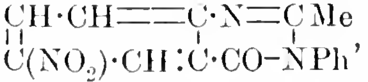
Marston T. Bogert and Ellen P. Cook (*J. Amer. Chem. Soc.*, 1906, **28**, 1449—1454. Compare this vol., i, 712, and earlier abstracts.)—5-*Nitroacetylanthranil*, $NO_2\cdot C_6H_3{<}\begin{matrix}NAc\\ |\\ CO\end{matrix}$, obtained by the action of acetic anhydride on 5-nitro-acetylanthranilic acid, crystallises in colourless needles and melts at 161—162° (corr.). By the action of dilute aqueous ammonia, it is converted into 6 nitro-4-keto-2-methyldihydroquinazoline (6-nitro-4-oxy-2-methylquinazoline), described by Dehoff (Abstr., 1891, 84) and by Thieme (Abstr., 1891, 917). When the anthranil is warmed with methylamine, it is converted into 6-nitro-4-keto-2 : 3-dimethyldihydroquinazoline (Dehoff and Thieme, *loc. cit.*).

6-*Nitro-4-keto-2-methyl-3-ethyldihydroquinazoline*,

$$\begin{array}{l}CH\cdot CH{=\!=\!=}C\cdot N{=}CMe\\ \|\qquad\qquad\quad |\qquad\ |\\ C(NO_2)\cdot CH{:}C\cdot CO{-}NEt\end{array},$$

obtained by the action of ethylamine on 5-nitroacetylanthranil, or by the action of ethyl iodide on the sodium derivative of the methylquinazoline, crystallises from alcohol in needles and melts at 166° (corr.).

6-*Nitro-4-keto-3-phenyl-2-methyldihydroquinazoline*,



$$\begin{array}{l}CH\cdot CH{=\!=\!=}C\cdot N{=}CMe\\ \|\qquad\qquad\quad |\qquad\ |\\ C(NO_2)\cdot CH{:}C\cdot CO{-}NPh\end{array},$$

separates from glacial acetic acid in small, pale yellow crystals, melts at 219—220° (corr.), and is sparingly soluble in alcohol.

6-*Nitro-3 amino-4-keto-2-methyldihydroquinazoline*,

$$\begin{array}{l}CH\cdot CH{=\!=\!=}C\cdot N{=}CMe\\ \|\qquad\qquad\quad |\qquad\ |\\ C(NO_2)\cdot CH{:}C\cdot CO{-}N\cdot NH_2\end{array},$$

obtained by heating 5-nitroacetylanthranil with hydrazine hydrate in 50 per cent. aqueous solution, crystallises in colourless needles, melts at 208—209° (corr.), and is readily soluble in dilute alcohol. It crystallises from glacial acetic acid with about 2/5 mol. of acetic acid.

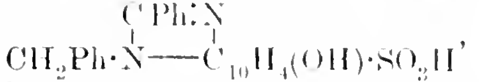
6 : 6′-*Dinitro-4 : 4′-diketo-2 : 2′-dimethyltetrahydrodiquinazolyl*,

$$\begin{array}{l}N{=}CMe\qquad\qquad\qquad CMe{:}N\\ |\qquad\quad {>}N\cdot N{<}\qquad\quad |\\ NO_2\cdot C_6H_3{-}CO\qquad\quad CO{-}C_6H_3\cdot NO_2\end{array},$$

obtained in small yield by heating 5-nitroacetylanthranil (2 mols.) with hydrazine hydrate (1 mol.) in 50 per cent. solution, separates from glacial acetic acid in small crystals containing 1 mol. of the solvent, and melts and darkens at 281—286°. E. G.

Preparation of 5-Hydroxynaphthabenzaldehydine-7-sulphonic Acid and its Diamino-derivative. Leopold Cassella & Co. (D R.-P. 172981).—1 : 2-Naphthylenediamine condenses with 2 molecular proportions of benzaldehyde to form naphthabenzaldehydine (Abstr., 1906, i, 536), but the reaction does not take place very readily. If, however, a hydroxysulphonic acid of the diamine is employed, the condensation is easily effected even in aqueous solutions.

5-*Hydroxynaphthabenzaldehydine-7-sulphonic acid*,



$$\begin{array}{c} \mathrm{CPh{:}N} \\ \vert \qquad\quad \vert \\ \mathrm{CH_2Ph\cdot N{-}{-}C_{10}H_4(OH)\cdot SO_3H} \end{array},$$

separates completely when benzaldehyde is added to 5 : 6-diamino-α-naphthol-3-sulphonic acid suspended in water, the mixture being stirred and heated until all the diamino-acid has disappeared. It is a yellow powder which forms a sodium salt crystallising in leaflets.

3′ : 5′-*Diamino-5-hydroxynaphthabenzaldehydine-7-sulphonic acid* is obtained directly by substituting *m*-aminobenzaldehyde for benzaldehyde in the foregoing condensation, or is obtained by reducing the corresponding nitro-compound obtained by using *m*-nitrobenzaldehyde in the condensation. On diazotising this diamine, a yellow bis-diazo-compound is produced which develops a red coloration with sodium carbonate solution. G. T. M.

Molecular Weight of Indigotin. Wilhelm Vaubel (*Ber.*, 1906, **39**, 3587—3588. Compare Abstr., 1901, i, 714; 1902, i, 110).—On recalculating the molecular weight of indigotin as determined cryoscopically in phenol (*loc. cit.*), with the aid of a correction for the maximum solubility of indigotin in the solvent, but with omission of that previously employed for the supposed absorption of water, the author finds his results to be entirely in agreement with those of Beckmann and Gabel (this vol., i, 900). G. Y.

Pyramidone Hydrochloride and Hydrobromide. Charles Astre and P. Aubouy (*Bull. Soc. chim*, 1906, [iii], **35**, 856—858).—*Pyramidone hydrochloride*, obtained by mixing a solution of hydrogen chloride in ether with the base dissolved in the same solvent, forms microscopic, colourless, prismatic crystals, melts at 143—144°, and is very hygroscopic, forming a syrupy acid liquid. The *hydrobromide*, similarly obtained, occurs in colourless, microscopic lamellæ, melts at 170—171°, and is very deliquescent, forming an acid liquid.

T. A. H.

***s*- and *as*-Phenosafranines.** Philippe Barbier and Paul Sisley (*Bull. Soc. chim.*, 1906, [iii], **35**, 858—868. Compare this vol., i, 51).—*s*-Phenosafranine can be diazotised much more rapidly than *as*-phenosafranine, and when an aqueous solution of its hydrochloride is shaken with chloroform, the latter does not become coloured as it does when a solution of *as*-phenosafranine hydrochloride is similarly treated, These differences in behaviour may be used to distinguish the two dyes.

The characters and solubilities of the nitrates and oxalates, and of the hydrates formed by the hydrochlorides and sulphates of the two isomerides, and the conditions under which these salts may be obtained are described in detail in the original. T. A. H.

Azophenols. Richard Willstätter and Max Benz (*Ber.*, 1906, 39, 3492—3503. Compare this vol., i, 997).—This paper contains the results of experiments devised to elucidate a curious case of isomerism among the azophenols. The *p*-azophenol obtained by reducing *p*-benzoquinoneazine differs from the substance prepared by the ordinary methods in its colour in the crystalline and powdered condition, in its behaviour towards moist air, and in its solubility in cold benzene. The new modification is denoted by the affix (*a*) and the older form by (*β*). It seems probable that these *a*- and *β*-compounds are geometrical isomerides. *p*-Azophenol (*a*) most conveniently prepared by fusing *p*-nitrophenol with potassium hydroxide, crystallises in a mono-hydrated form from ether or alcohol forming pale brown, or amber-yellow plates with blue reflex. The solubility of the hydrated form in benzene at 17° is 1 in 10,800; the anhydrous form separates from this solvent in cruciform aggregates of greenish-brown crystals. The powdered *a*-compound assumes a dark yellow colour which becomes green on heating. Both hydrated and anhydrous forms melt and decompose at 215°. A glacial acetic acid solution of hydrogen bromide furnishes blue crystals of the *hydrobromide*, $C_{12}H_{10}N_2,HBr$.

p-*Azophenol* (*β*), prepared by reducing *p*-benzoquinoneazine with phenylhydrazine in benzene solution, forms dark red, and reddish-brown leaflets with a blue reflex; when powdered it is brownish-red with a blue tinge, and at 110—140° it assumes a brick-red colour. The solubility of the *β* compound in benzene at 17° is 1 in 1500. On heating a portion of the *β*-compound under reduced pressure a small yield of the green pulverulent anhydrous *a*-modification is obtained. The *a*-compound is partially converted into the *β*-modification by heating with moist ether. The two isomerides behave similarly towards dry ammonia gas, yielding anhydrous diammonium salts, which completely dissociate in the air or in the desiccator; they are oxidised with equal readiness by silver oxide, and are equally stable towards phenylhydrazine, with which they each combine to form a crystallisable *salt*,

$$C_{12}H_{10}O_2N_2,C_6H_8N_2.$$

o-Azophenol, when prepared by the potash fusion method from *o*-nitrophenol is accompanied by a by-product, triphenodioxazine,

$$C_{18}H_{10}O_2N_2.$$

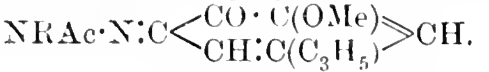
The *o*-azo-compound takes up 1 mol. of ammonia to form a coffee-brown ammonium salt; if, however, it has been previously melted or distilled in a vacuum, it does not show any tendency to combine with dry ammonia, but regains the power on recrystallisation or exposure to an atmosphere of damp ammonia. *m*-Azophenol, which combines with a proportion varying between 1 and 2 mols. of ammonia, does not react in ethereal solution with silver oxide. G. T. M.

Derivatives of 5-Azoeugenol and the Constitution of the so-called *o*-Hydroxyazo-compounds. GIUSEPPE ODDO and ERNESTO PUXEDDU (*Gazzetta*, 1906, 36, ii, 1—48. Compare Abstr., 1905, i, 492, this vol., i, 774).—After reviewing the present state of knowledge of the hydroxyazo-compounds, the properties of the following azo-compounds derived from eugenol are discussed at some length. The principal conclusions arrived at are as follows.

All the azoeugenols are nearly insoluble in cold 0·5 per cent. aqueous sodium hydroxide, but dissolve much more readily in the same liquid at 100°. No change in the boiling point of the sodium hydroxide solution occurs on adding successive quantities of the azo-compound; this behaviour, which is also shown by phenol and *a*-naphthol, is held to prove that the azoeugenols yield true sodium salts, which are dissociated to almost the same extent as sodium hydroxide. On cooling the solutions, the sodium salts undergo hydrolysis to the extent of about 58—92 per cent., depending on their structure, the original azoeugenol separating in crystals. No simple connexion can be traced between the degree of hydrolysis of the salts and their solubility. The hydrolysis is held to show that the azoeugenols are pseudo-acids, giving salts only in virtue of a molecular change; they do not redden litmus or combine with ammonia in dry benzene. From their chemical behaviour the free azoeugenols appear to be neither hydrazones nor carbonyl compounds. When boiled with acids or alkalis they do not undergo hydrolysis to form a corresponding quinone; and although they interact vigorously with phenylhydrazine at 110° the product is never a dihydrazone, but always aminoeugenol formed by reduction. Such a reducing action is not observed when ordinary aromatic phenylhydrazones are heated with phenylhydrazine. With hydroxylamine the azoeugenols fail to interact.

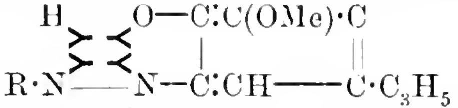
The behaviour of the azoeugenols when treated with sodium ethoxide and subsequently with ethyl iodide in alcoholic solution, depends on the nature of the aromatic radicle attached to the azo-group. *o*-Tolueneazoeugenol, *as*-*m*-xyleneazoeugenol, and *p*-xyleneazoeugenol do not form ethers; these substances contain a methyl radicle in the ortho position relatively to the azo-group. Benzeneazoeugenol, *m*-tolueneazoeugenol, and *p*-bromobenzeneazoeugenol, give unstable ethers which are at once hydrolysed at the ordinary temperature by 0·5 per cent. aqueous sodium hydroxide. Azoeugenols containing negative elements or radicles in any position (with the exception of *p*-bromobenzeneazoeugenol) give well-defined ethers, which are hydrolysed only by warm sodium hydroxide. The ethers differ entirely from the parent azoeugenols in their behaviour with phenylhydrazine; no action occurs at 110° and very little at 170—180°. In no case is aminoeugenol ethyl ether formed. The ethyl ethers of the azoeugenols appear to have the structure,

$R\cdot N{:}N\cdot C{<}\begin{matrix}C(OEt)\cdot C(OMe)\\ CH{=\!=}C(C_3H_5)\end{matrix}{>}CH$, of true oxygen ethers.

The acetyl derivatives of the azoeugenols are in all cases easily prepared, and are decomposed only slowly by boiling aqueous sodium hydroxide. Like the parent azoeugenols they interact readily with phenylhydrazine at 110—120°, undergoing reduction to aminoeugenol; acetylaminoeugenol is never formed. The acetyl derivatives thus differ entirely from the ethyl ethers, and cannot have an analogous structure; the behaviour with phenylhydrazine is moreover held to exclude the structure  $NRAc{\cdot}N{:}C{<}{\genfrac{}{}{0pt}{}{CO{\cdot}C(OMe)}{CH{:}C(C_3H_5)}}{\gg}CH$. The structure

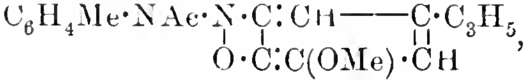
however, is advocated as explaining the properties of the acetyl derivatives.

The parent hydroxyazo-compounds are considered to correspond in structure neither with the alkyl ethers nor with the acetyl derivatives. The formula,



, is attributed to the free hydroxyazo-compounds, it being assumed that an ordinary single bond can, in certain cases, be divided between two neighbouring elements, as indicated by the sign $\prec$ in the formula. These compounds are termed *mesohydric* and names such as *benzenemesohydrazoeugenol* for benzeneazoeugenol, are given to them.

o-*Tolueneazoeugenol* (o-*toluenemesohydrazoeugenol*), prepared from the *o*-diazotoluene chloride and sodium eugenoxide (compare Abstr., 1905, i, 492), crystallises from alcohol in dark red, prismatic needles, melts at 92—93°, and gives an *acetyl* derivative,



which crystallises from light petroleum in small, lustrous needles, melts at 72—73°, and is reduced by tin and hydrochloric acid to amino-eugenol.

m-*Tolueneazoeugenol* forms small, dark red plates, and melts at 79—80°; the *acetyl* derivative forms orange-red needles and melts at 81°; m-*tolueneazoeugenol ethyl ether* was obtained only as an oil.

p-*Tolueneazoeugenol* forms rosettes of dark red needles, melts at 102—103°, and gives an *acetyl* derivative which crystallises in carmine needles and melts at 110—112°; p-*tolueneazoeugenol ethyl ether* crystallises from dilute alcohol in red prisms or pyramids and melts at 55°.

as-m-*Xyleneazoeugenol*, prepared from diazotised *as-m*-xylidine, forms red needles and melts at 108°; the *acetyl* derivative forms orange-red needles and melts at 104—105°.

p-*Xyleneazoeugenol*, prepared from *p*-xylidine, forms reddish-brown crystals and melts at 97°; the *acetyl* derivative melts at 88°.

o-*Nitrobenzeneazoeugenol*, prepared from diazotised *o*-nitroaniline, crystallises in lustrous, brown spangles or needles, melts at 143°, and gives an *acetyl* derivative which forms dark red needles and melts at 124°; o-*nitrobenzeneazoeugenol ethyl ether* forms orange-red plates and melts at 72—73°. m-*Nitrobeneazoeugenol* crystallises from alcohol in needles, melts at 106—107°, and gives an *acetyl* derivative which forms orange-red crystals and melts at 112°; the *ethyl ether* crystallises from alcohol in reddish-orange scales and melts at 86°.

m-Bromobenzeneazoeugenol (*loc. cit.*) melts at 100°, not at 96°, as previously stated; its *ethyl ether* crystallises from alcohol in flattened, orange-red prisms and melts at 100—101°. p-*Chlorobenzeneazoeugenol* forms rusty-red needles, melts at 117°, and gives an *acetyl* derivative which crystallises in reddish-yellow needles and melts at 113°. p-*Chlorobenzeneazoeugenol ethyl ether* crystallises in silky, reddish-yellow needles and melts at 65°. p-*Bromobenzeneazoeugenol* forms dark-red prisms and melts at 123—124°; the *acetyl* derivative forms orange prisms and melts at 123°. 2 : 4-*Dichlorobenzeneazoeugenol*, prepared from 2 : 4-dichloroaniline, forms rust-coloured crystals and melts at 130°; the *acetyl* derivative forms reddish-brown needles and melts at 156°. W. A. D.

Action of Sulphurous Acid on Diazo-*m*-toluene Chloride and Sulphate. Julius Tröger and F. Schaub (*Arch. Pharm.*, 1906, **244**, 302—307. Compare this vol., i, 120).—In order to obtain the sulphonic acid, $C_{14}H_{16}O_3N_4S$, or $C_6H_4Me\cdot N{:}N\cdot C_6H_3Me\cdot NH\cdot NH\cdot SO_3H$, in the pure state, the crude acid resulting from the action of sulphur dioxide on an aqueous diazo-*m*-toluene salt should be extracted with boiling water and then dried in a vacuum until constant in weight. Yellow to brown potassium, sodium, ammonium, *aniline*, p-*toluidine*, and p-*xylidine* salts were prepared by adding the acid to concentrated solutions of the acetates of the bases, adding so much water in the first three cases, or alcohol in the last three, that the precipitate dissolves on heating, filtering the solution, and allowing it to crystallise; the last three salts melt and decompose at 151—152°, 154°, and 165° respectively. C. F. B.

Action of Sulphurous Acid on Diazobenzene Sulphate. Julius Tröger and M. Franke (*Arch. Pharm.*, 1906, **244**, 307—312. Compare this vol., i, 120).—In presence of a large amount of sulphuric acid a diazo-sulphite is formed; when relatively less sulphuric acid is present, the sulphonic acid $C_{12}H_{12}O_3N_4S$, or

$$NPh{:}N\cdot C_6H_4\cdot NH\cdot NH\cdot SO_3H$$

is the product; in the presence of still more water, sulphazide, $NHPh\cdot NH\cdot SO_2Ph$, is produced.

The crude sulphonic acid was obtained by diazotising a solution of 15 grams of aniline in 300—500 grams of water and 50 grams of concentrated sulphuric acid, and passing sulphur dioxide into the diazo-solution, kept well cooled. It was purified by adding it to a solution of ammonium acetate, diluting with so much water that the precipitate dissolved on heating, filtering the solution while hot, acidifying with dilute sulphuric acid, and allowing it to cool. The yellow to brown *ammonium*, *aniline*, p-*toluidine*, and p-*xylidine* salts were prepared in the way described in the preceding abstract; the last three melt and decompose at about 165°, 172°, and 177° respectively. C. F. B.

Probable Constitutional Formula of the Sulphonic Acid, $C_{14}H_{16}O_3N_4S$, formed by the Action of SO_2 on Diazo *m*-toluene. Julius Tröger, G. Warnecke, and F. Schaub (*Arch. Pharm.*, 1906, **244**, 312—325. Compare this vol. i, 120, and preceding abstracts).—The acid has the character of a hydrazine derivative,

$$C_6H_4Me\cdot N{:}N\cdot C_6H_3Me\cdot NH\cdot NH\cdot SO_3H.$$

Ammoniacal silver and copper solutions convert it, and mercuric oxide converts its potassium salt, into the *silver*, *ammonium*, and *potassium* salts respectively of an *acid* containing two atoms of hydrogen less in the molecule, $C_6H_4Me\cdot N{:}N\cdot C_6H_3Me\cdot N{:}N\cdot SO_3H$; this acid was only obtained as a syrup, which was converted into the *sodium* salt.

When the first sulphonic acid is treated with an aromatic aldehyde, $C_6H_4X\cdot CHO$, in glacial acetic acid, or in alcohol containing a little sulphuric or acetic acid, the sulphonic group is eliminated and a blue or green *sulphate* is obtained, from which ammonia liberates a red or brown *base*. The latter substance may be a hydrazone,

$$C_6H_4Me\cdot N{:}N\cdot C_6H_3Me\cdot NH\cdot N{:}CH\cdot C_6H_4X;$$

or it may have been produced by the condensation of two molecules of the hydrazine with one of the aldehyde $(C_{14}H_{15}N_4)_2CH\cdot C_6H_4X$, as in the case of salicylaldehyde already described. The investigation of these substances is difficult; both of them may be formed at the same time, and the conditions favouring the formation of each have not yet been ascertained. Benzaldehyde and salicylaldehyde, $(X = H,OH)$, form both a *hydrazone*, melting in the former case at 159—160°, and a trimolecular condensation *product*, melting in the latter case at 130°; *m*- and *p*-nitrobenzaldehydes, $(X = NO_2)$ form only *hydrazones*, which melt at 177° and 160—161° respectively; and cinnamaldehyde, forms only a termolecular condensation *product* melting at 124°. *m*-Bromobenzaldehyde yields a *base* melting at 137° of which the constitution has not yet been elucidated. C. F. B.

Probable Constitutional Formula of the Sulphonic Acid, $C_{12}H_{12}O_3N_4S$, formed by the Action of SO_2 on a Diazobenzene Salt. JULIUS TRÖGER, H. BERLIN, and M. FRANKE (*Arch. Pharm.*, 1906, **244**, 326—335. Compare this vol., i, 120, and the preceding abstracts).—The acid has the character of a hydrazine derivative, $C_6H_5\cdot N{:}N\cdot C_6H_4\cdot NH\cdot NH\cdot SO_3H$. Ammoniacal silver and copper solutions convert it respectively into the *silver* and *ammonium* salts of an acid containing two atoms of hydrogen less in the molecule, $C_6H_5\cdot N{:}N\cdot C_6H_4\cdot N{:}N\cdot SO_3H$.

The first acid condenses, when suspended in glacial acetic acid and treated with aromatic aldehydes, $C_6H_4X\cdot CHO$, to yellow or red *hydrazones*, $C_6H_5\cdot N{:}N\cdot C_6H_4\cdot NH\cdot N{:}CH\cdot C_6H_4X$; these have the character of mono-acid bases, and unite with the sulphuric acid (produced by the elimination of the sulphonic group) to form a blue or green *sulphate*, which is decomposed more or less by hot water, completely by ammonia. No products were obtained that proceeded from the condensation of two molecules of the hydrazinesulphonic acid with one of the aldehyde. Hydrazones were obtained with benzaldehyde, *m*- and *p*-nitrobenzaldehydes, salicylaldehyde, anisaldehyde,

$$(X = H,\ NO_2,\ NO_2,\ OH,\ OMe),$$

and cinnamaldehyde; they melt at 168·5—169°, 198—199°, 173°, 206°, 132°, and 167° respectively. C. F. B.

Condensation of the Three Nitroanilines with *p*-Nitrosobenzaldehyde. FREDERICK J. ALWAY and ROSS A. GORTNER (*Amer. Chem. J.*, 1906, **36**, 510—515).—The ease with which the nitroanilines condense with *p*-nitrosobenzaldehyde varies with their basicity; thus, *m*-nitroaniline condenses readily, *p*-nitroaniline less readily, and *o*-nitroaniline so feebly that the condensation product could not be isolated.

The m-*nitroanil* of m-*nitrobenzene*-p-*azobenzaldehyde*,

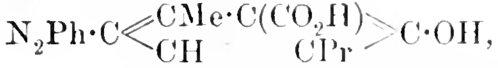
$$NO_2\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot CH{:}N\cdot C_6H_4\cdot NO_2,$$

obtained by the condensation of *m*-nitroaniline with *m*-nitrosobenzaldehyde, forms brick-red, granular masses, melts at 239·5° (corr.), is readily soluble in nitrobenzene and sparingly so in alcohol or glacial acetic acid, and by prolonged treatment with hot, dilute hydrochloric acid is resolved into *m*-nitrobenzene-*p*-azobenzaldehyde and *m*-nitroaniline. m-*Nitrobenzene*-p-*azobenzaldehyde* crystallises in minute, red needles, melts at 135° (corr.) and is very soluble in alcohol, glacial acetic acid, or nitrobenzene; the substance previously described under this name (Abstr., 1904, i, 953) contained a large proportion of the *m*-nitroanil. The *phenylhydrazone* of *m*-nitrobenzene-*p*-azobenzaldehyde crystallises in dark red, rectangular plates and melts at 213·5 (corr.). The *oxime* separates from dilute alcohol in yellow crystals and melts at 116° (corr.). The *anil* forms small yellow crystals, and melts at 132° (corr.).

The p-*nitroanil* of p-*nitrobenzene*-p-*azobenzaldehyde* crystallises in small red needles, melts at 237—238·5° (corr.), and is sparingly soluble in alcohol but readily so in hot acetic acid. p-*Nitrobenzene* p-*azobenzaldehyde* crystallises in long, red plates, melts at 221—222° (corr.), and is very soluble in hot benzene, glacial acetic acid, nitrobenzene, or amyl alcohol. The *anil* forms stellate groups of orange-coloured needles, melts at 152° (corr.), and is insoluble in alcohol. The *oxime* is a yellow solid which does not melt below 290°. E. G.

Reduction of Azo-derivatives of Aromatic Hydroxy-acids by Phenylhydrazine.

ERNESTO PUXEDDU (*Gazzetta*, 1906, **36**, ii, 305—313).—*Benzeneazo*-o-*thymotic acid*,



$$N_2Ph\cdot C{<}\begin{matrix}CMe\cdot C(CO_2H)\\ CH \qquad\quad CPr\end{matrix}{>}C\cdot OH,$$

prepared by the action of diazobenzene sulphate on *o*-thymotic acid dissolved in sodium hydroxide solution, crystallises from alcohol or benzene in orange-yellow, prismatic needles melting at 185—195°, and dissolves in the more common organic solvents. It gives an intensely reddish-brown coloration with ferric chloride, dissolves in concentrated sulphuric acid to a cherry-red, in concentrated hydrochloric acid to a straw-yellow liquid, and in alkali solutions to a blood-red liquid. When it is reduced by means of phenylhydrazine, the N_2Ph group is doubtless replaced by NH_2, but the compound thus formed loses carbon dioxide, giving the corresponding aminothymol melting at 178°.

The reduction of benzeneazo-*m*-hydroxybenzoic acid by means of phenylhydrazine proceeds with explosive violence, and yields 6-amino-3-hydroxybenzoic acid.

o-*Tolueneazo*-m-*hydroxybenzoic acid*, $C_{14}H_{12}O_3N_2$, crystallises from alcohol in yellow, prismatic needles melting at 240°, and dissolves readily in the more common organic solvents. It is completely insoluble in dilute acids, but dissolves in concentrated acids, giving, with nitric acid, a deep red colour, disappearing on heating, and with sulphuric acid an intense blackish-brown liquid. Reduction with phenylhydrazine yields 6-amino-3-hydroxybenzoic acid.

p-*Tolueneazo*-m-*hydroxybenzoic acid*, $C_{14}H_{12}O_3N_2$, crystallises from alcohol or a mixture of alcohol and benzene in shining, prismatic needles, and melts and decomposes at 233°. It dissolves in organic solvents, in dilute alkali solutions, and in concentrated acids, being reprecipitated from the last-named by addition of water. Its reduction by means of phenylhydrazine proceeds explosively, and yields 6-amino-3-hydroxybenzoic acid.

m-*Chlorobenzeneazo*-m-*hydroxybenzoic acid*, $C_{13}H_9O_3N_2Cl$, crystallises from alcohol in orange-red, prismatic needles melting at 225—227°, and is soluble in concentrated acids, dilute alkali solutions, or organic solvents. Its reduction with phenylhydrazine takes place with explosive violence and yields 6-amino-3-hydroxybenzoic acid.

p-*Chlorobenzeneazo*-m-*hydroxybenzoic acid* crystallises from alcohol in orange-yellow, prismatic needles melting and decomposing at 235—236° and is soluble in organic solvents, concentrated acids, or dilute alkali solutions. When reduced with phenylhydrazine, it gives 6-amino-3-hydroxybenzoic acid. T. H. P.

The Oxidation of Benzidine. RICHARD WILLSTÄTTER and LUDWIG KALB (*Ber.*, 1906, **39**, 3474—3482).—This investigation was undertaken with the object of ascertaining the nature of a yellow, crystalline oxidation product of benzidine, obtained by oxidising the diamine with silver oxide or lead peroxide in inert solvents. This object has been attained by preparing the substance synthetically from 4-nitro-4′-aminodiphenyl, the *acetyl* derivative of which crystallises in prisms and melts at 240°.

4 : 4-Diamino-4′ : 4′-azodiphenyl, $N_2(C_6H_4\cdot C_6H_4\cdot NH_2)_2$, obtained by reducing 4-nitro-4′-aminodiphenyl with zinc dust and alcoholic sodium hydroxide, corresponds in every respect with the product of the oxidation of benzidine (Abstr., 1905, i, 361); it crystallises in microscopic, yellowish-red needles, melts at 287°, and develops a characteristic blood-red coloration with concentrated sulphuric acid. The salts of this base with the mineral acids are insoluble in water; the *monohydrochloride*, $C_{24}H_{20}N_4,HCl$, consists of small, brown prisms; the *dihydrochloride*, $C_{24}H_{20}N_4,2HCl$, is amorphous.

s-*Diacetyl*-4 : 4-*diamino*-4′ : 4′-*azodiphenyl*, produced from the diamine by the action of acetic anhydride, melts indefinitely and decomposes at 373°.

Tetra-azo-azodiphenyl chloride, $N_2(C_6H_4\cdot C_6H_4\cdot N_2Cl)_2,2H_2O$, is produced most readily by diazotising the corresponding diamine with a large excess of hydrochloric acid (1 per cent.) and aqueous sodium nitrite (10 per cent.), when the salt is precipitated from the clear solution thus obtained by the addition of concentrated hydrochloric acid. The chloride, which consists of prismatic crystals having a violet reflex, gives an orange-red streak; it is moderately stable in air, and decomposes violently at about 95°. The tetra-azo sulphate and nitrate are both crystalline, the latter being exceptionally insoluble; the *platinichloride*, $C_{24}H_{16}N_6PtCl_6,H_2O$, is an insoluble, yellow, flocculent precipitate. G. T. M.

Action of Diazo-compounds on α-Hydroxynaphthoic Acids. EUGÈNE GRANDMOUGIN (*Ber.*, 1906, 39, 3609—3611. Compare Nietzki and Guitermann, Abstr., 1887, 732; Reverdin and De la Harpe, Abstr., 1893, i, 478).—The action of diazobenzene chloride on 1-hydroxy-2-naphthoic acid in alkaline solution, leads to the formation of dibenzeneazo-α-naphthol (Noelting and Grandmougin, Abstr., 1891, 1076), which is formed also by the action of diazobenzene chloride on benzeneazo-1-hydroxy-2-naphthoic acid.

The reduction of benzeneazo-1-hydroxy-2-naphthoic acid by means of sodium hyposulphite in aqueous alcoholic solution (compare this vol., i, 716) leads to the formation of aniline and 4-amino-1-hydroxy-2-naphthoic acid (Nietzki and Guitermann, *loc. cit.*), which crystallises in slender, colourless needles, forms a crystalline *hydrochloride*, and yields 4-amino-α-naphthol when heated in a current of hydrogen chloride, or naphthaquinone when treated with nitrous acid. Aniline and 3 : 4-diamino-α-naphthol are obtained by reduction of dibenzeneazo-α-naphthol by means of sodium hyposulphite. G. Y.

Quinoneazines. By RICHARD WILLSTÄTTER and MAX BENZ (*Ber.*, 1906, 39, 3482—3491).—4 : 4′-Dihydroxydiphenyl and 4 : 4′-dihydroxystilbene resemble catechol in being oxidised to quinonoid substances by silver oxide or lead peroxide, but 4 : 4′-dihydroxydiphenylmethane does not exhibit this behaviour. Hence it appears that the ethylene linking $\cdot CH{:}CH\cdot$ does not sever completely the quinonoid relationship between the two benzene nuclei, whereas this connexion is quite annulled by the interposition of the methylene group. It is now shown that the azo-group is analogous to the ethylene group, the *p*-azophenols undergoing the characteristic oxidation.

p-*Benzoquinoneazine*, $O{:}C_6H_4{:}N\cdot N{:}C_6H_4{:}O$, prepared by shaking an ethereal solution of *p*-azophenol with silver oxide and fused sodium sulphate, crystallises from organic solvents either in dark orange-red prisms or needles or in dark yellow, rhombohedral leaflets or plates; both modifications have a blue reflex. When treated in dry ethereal solution with concentrated sulphuric acid the quinoneazine yields *p*-azophenol and an easily decomposable base; sulphurous acid or preferably phenylhydrazine reduces the quinoneazine to an azophenol which is not identical with ordinary *p*-azophenol.

The *quinhydrone*, $C_{24}H_{18}O_4N_4$, of *p*-benzoquinoneazine separates in bluish-black needles with a bronze reflex on mixing ethereal solutions of *p*-azophenol and the quinoneazine; it melts at 181—182° and undergoes dissociation in alcoholic solution.

4 : 4′-Dihydroxystilbene when oxidised with lead peroxide or potassium ferricyanide gives rise to stilbenequinone, which is again reduced by phenylhydrazine to the original dihydroxy-compound.

p-*Acetylaminodiazoaminobenzene*, $C_6H_5\cdot NH\cdot N_2\cdot C_6H_4\cdot NHAc$, the intermediate product of the interaction of diazoacetanilide and aniline, crystallises in orange-yellow, acicular prisms and melts and decomposes at 150—152°.

p-*Aminodiazoaminobenzene*, $C_6H_5\cdot NH\cdot N_2\cdot C_6H_4\cdot NH_2$, obtained by hydrolysing the foregoing compound with sodium ethoxide, crystallises from dilute alcohol in brownish-yellow needles decomposing at 157°. Azoaniline, which is produced together with a preponderating amount of aminoazobenzene by warming the foregoing diazoamine with aniline and aniline hydrochloride, does not undergo the quinonoid oxidation on treatment with silver oxide or lead peroxide. G. T. M.

Ash-free Egg Albumin. R. W. Rosenkrantz (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, i, 2—3).—Crystals of egg-albumin obtained by a modification of the Hofmeister-Krieger process, are crystallised 6 to 10 times. They are then dissolved, dialysed, evaporated in a vacuum and again dialysed. Preparations so obtained give no ash on ignition, and do not contain recognisable quantities of ammonium sulphate. Z. K.

Complexes of Pure Albumin. André Mayer (*Compt. rend.*, 1906, **143**, 515—516).—Pure ovalbumin, obtained from white of egg by diluting with water, filtering the precipitated globulins, recovering the albumin by prolonged dialysis, and repeating the processes several times, has a specific electrolytic conductivity of $1\cdot10^{-5}$, is not coagulated by heat, but forms soluble complexes with acids, (HCl, HNO_3, H_2SO_4), bases ($NaOH$, KOH), or salts [$NaCl$, KCl, $MgCl_2$, $CaCl_2$, $(NH_4)_2SO_4$, $MgSO_4$, Na_2SO_4, K_2SO_4]. The amount of electrolyte absorbed by a definite quantity of ovalbumin, to raise the electrolytic conductivity from $1\cdot10^{-5}$ to $1\cdot10^{-4}$ varies with the nature of the electrolyte, being greater in the case of the acids than the bases or univalent salts, and greater in the case of the univalent than the bivalent salts. Ovalbumin forms insoluble complexes with salts of the heavy metals or positive colloids, which are soluble in dilute solutions of electrolytes and for this purpose $N/160$, HCl; $N/140$, NaOH; or $N/30$, NaCl are equivalent; from the solution a precipitate is formed by dilution or by dialysis, and the solution is coagulated by heating, the temperature at which coagulation occurs varying with the nature of the electrolyte used as the solvent. Thus a solution of an albumin-zinc salt coagulated at 56°, 60°, or 86°, according as it had been dissolved in hydrochloric acid, sodium chloride, or potassium hydroxide respectively. In respect of all these properties, the insoluble albumin complexes closely resemble the globulins, which may be regarded as complexes of pure albumin. M. A. W.

Distinction between Serum-albumin and Myo-albumin. Joseph de Rey-Pailhade (*Bull. Soc. chim.*, 1906, [iii], **35**, 1030—1031. Compare Abstr., 1904, i, 837; 1905, i, 728).—Aqueous extracts of the muscle of the cow, calf, horse, or turkey, and of whiting, evolve hydrogen sulphide on addition of sulphur, and this property is also exhibited by the coagulated albumins obtained by heating these extracts. The insoluble white residue, left after repeatedly washing horse-muscle with water, is almost inactive towards sulphur, and appears to behave as an inactive reserve for the more active and soluble myo-albumin. The latter is rendered inactive by contact with sulphur for several days, and the coagulum obtained from this is similarly inactive towards sulphur. An analogous non-philothionic myo-albumin may be obtained by extracting the uterus of the sheep with dilute alcohol; the fresh tissue furnishes traces of hydrogen sulphide with sulphur, but the coagulum obtained by heating the alcoholic extract gives none. T. A. H.

Philothionic Hydrogen. JOSEPH DE REY-PAILHADE (*Bull. Soc. chim.*, 1906, [iii], 35, 1031—1033. Compare preceding abstract and Heffter and Hausmann, Abstr., 1904, i, 461).—The philothionic hydrogen of myo-albumin is not destroyed after 15 days' exposure to air at the atmospheric temperature, whereas it is much more rapidly removed by sulphur (see preceding abstract). In this connexion it is pointed out that hydrogen and sulphur combine at 250°, whereas hydrogen and oxygen do not unite below 350°, and it is suggested that whilst philothion seems to be capable of effecting the same chemical change as is induced by an increase in temperature of about 250°, its activity is insufficient to cause a combination which requires an increase of 350°. T. A. H.

Monoamino-acids of the Crystalline Proteid from Pumpkin Seeds. EMIL ABDERHALDEN and OSCAR BERGHAUSEN (*Zeit. physiol. Chem.*, 1906, 49, 15—20).—The substances obtained from the cleavage of edestin (vitellin) by means of dilute sulphuric acid were: glycine, 0·08; alanine, present; aminovaleric acid, 0·7; leucine, 4·7; proline, 1·7; glutamic acid, 13·4; aspartic acid, 4·5; phenylalanine, 2·6; and tyrosine, 1·4 per cent. W. D. H.

Optical Rotation of Gliadin in Certain Organic Solvents. W. E. MATHEWSON (*J. Amer. Chem. Soc.*, 1906, 28, 1482—1485. Compare this vol., i, 545).—The specific rotatory powers of solutions of gliadin in methyl, ethyl, propyl, and benzyl alcohols, phenol, *p*-cresol, and glacial acetic acid have been determined, and the results are tabulated. The gliadin was prepared from wheat-flour, and the experiments were made in connexion with an investigation which is in progress with a view to the improvement of the methods of flour analysis. E. G.

Iodospongin. Preliminary Note. L. SCOTT (*Chem. Centr.*, 1906, ii, 1133; from *Biochem. Zeit.*, 1906, 1, 367).—The non-digestible residue of sponge substance can be rendered soluble by treatment with concentrated sulphuric acid. The product is then digested with pancreatic juice until it no longer gives the biuret reaction. After separating the diamino-acids, an organic compound, rich in iodine, is obtained, which is purified from monoamino-acids by the fractional crystallisation of its copper salt. P. H.

The Rendering Insoluble of Gelatin by Formaldehyde. AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and ALPHONSE SEYEWETZ (*Bull. Soc. chim.*, 1906, [iii], 35, 872—879. Compare this vol., i, 614, 915).—When gelatin is soaked in a solution of formaldehyde, the insoluble product formed contains from 4 to 4·8 per cent. of the aldehyde. The rapidity with which the formaldehyde is absorbed under these conditions increases with the concentration of the solution, but is not sensibly influenced by increase of temperature. Gaseous formaldehyde is absorbed more slowly by gelatin, but the product ultimately formed is similar to that obtained in the first case. The precipitate produced by mixing solutions of gelatin and formaldehyde contains unaltered gelatin.

Gelatin rendered insoluble by formaldehyde is slowly decomposed by hot water, and the formaldehyde may be completely eliminated by this means. The same decomposition is brought about by macerating the product in cold, dilute hydrochloric acid, and this method was used for the liberation and ultimate estimation of the formaldehyde by Seyewetz and Gibello's process (Abstr., 1904, ii, 521). The formaldehyde is also gradually liberated from the insoluble product when the latter is heated at 110°. From these results it is concluded that when gelatin is treated with formaldehyde, an additive product rather than a true compound is formed. T. A. H.

Intramolecular Absorption of Water in the Tryptic Digestion of Proteid. PAUL HÁRI (*Pflüger's Archiv*, 1906, **115**, 52—63).—Elementary analysis shows that the products (peptone) of the action of trypsin on proteids contain more oxygen and more hydrogen than the original material. This is attributed to the intramolecular absorption of water. W. D. H.

Tryptophan. CARL NEUBERG (*Chem. Centr.*, 1906, ii, 892; from *Charité Ann.*, **30**).—The author suggests the following modification of Hopkins and Cole's method of preparing tryptophan. In the second precipitation with mercuric sulphate the first portions, consisting almost entirely of cystine and mercury-cysteine, should be rejected; the filtrate is then treated with hydrogen sulphide, and after boiling off the excess of the latter, an excess of lead carbonate is added (100 grams of lead carbonate per kilogram of casein). The whole is then warmed on a water-bath for half an hour, ammonia is added until the solution smells faintly, and the heating is continued for a quarter of an hour more. The dissolved lead is then precipitated by means of hydrogen sulphide and the solution is evaporated; perfectly pure, white tryptophan separates out in a yield of 7—8 grams per kilogram of well-digested casein. P. H.

Myelin Bodies. J. G. ADAMI and L. ASCHOFF (*Proc. Roy. Soc.*, 1906, **78** B, 359—368).—The term myelin was originally applied by Virchow to a constituent of the white substance of nerves which swells up with water, and develops curious forms with a double contour. Myelin bodies have since then been described in many situations in cell protoplasm under both physiological and pathological conditions. Many soaps exhibit the same phenomena. The globules formed are doubly refracting, and the hypothesis is advanced that they are fluid sphærocrystals. With regard to their chemical composition there is still much doubt, but the evidence appears to point to two principal varieties, namely, cholesterol oleate and choline oleate. W. D. H.